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Diblock and Triblock Copolymers as Nanostructured Precursors to Functional Nanoporous Materials: From Design to Application

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Abstract:

Block copolymers have gained a tremendous interest from the scientific community in the last two decades. These macromolecular architectures indeed constitute ideal nanostructured precursors for the generation of nanoporous materials meant for various high added value applications. The parallel emergence of controlled polymerization techniques has notably enabled to finely control their molecular features to confer them with unique structural and physico-chemical properties, such as low dispersity values (\bar{D}), well defined volume fractions, and controlled functionality. The nanostructuring and ordering of diblock or triblock copolymers, that can be achieved through various experimental techniques, including channel die processing, solvent vapor or thermal annealing, non-solvent-induced phase separation or concomitant self-assembly and non-solvent-induced phase separation, allows for the preparation of orientated microphase-separated copolymers whose morphology is dictated by three main factors, *i.e.* Flory-Huggins interaction parameter between constitutive blocks, volume fraction of the blocks, and polymerization degree. This review article provides an overview of the actual state of the art regarding the preparation of functional nanoporous materials from either diblock or triblock copolymers. It will also highlight the major applications of such peculiar materials.

Keywords: Block Copolymer, Functionalized junction, Functionality, Nanoporous material, Nanostructuring

1. Introduction

Over the last decades, porous materials have attracted much attention from the scientific community. Such materials, either organic, inorganic or hybrid, present some inherent properties that make them attractive for high added-value applications. They have been notably implemented in heterogeneous supported catalysis, (nano)filtration and separation techniques, phonic and thermic isolation, template-assisted synthesis of nanomaterials, nanolithography, microelectronics, and photovoltaics, to cite but a few. Among the wide diversity of porous materials, those prepared from natural or synthetic polymers present some undeniable advantage over their hybrid or inorganic counterparts that render them particularly appealing for the scientific community. Indeed, they are firstly prepared through low-cost chemical processes. Additionally, they can be more easily functionalized with a biological or an organic molecule when compared to their inorganic or hybrid counterparts. Moreover, they also possess tunable mechanical properties in a useful range. In this regard, material scientists have developed a plethora of synthetic strategies allowing for the design of such porous frameworks that depend on the targeted pore size and morphology notably.

The basic idea underlying the design of (nano)porous polymers relies on the introduction of several types of porogens (solvents, gases, (macro)molecules) within polymer structures, followed by their selective removal. Solvents and gases used as porogens create pores by physically- or chemically induced phase separation, but the microstructures of the resulting materials are characterized by a broad pore size distribution. In contrast, the utilization of suitable porogen templates enables the generation of nanoporous polymers with a defined porosity. Distinct types of simple organic molecules and specific macromolecules have thus been used as effective porogen templates for creating a wealth of nanoporous materials with desired characteristics. These elegant template-oriented strategies mainly include molecular imprinting,¹ selective removal of a porogen homogeneously blended within a thermostable matrix,² selective removal of one partner from (semi-)Interpenetrating Polymer Networks (IPNs),³ selective degradation of block copolymers (BCPs),⁴ and selective destruction of supramolecular assemblies.⁵

Especially, the preparation of nanoporous polymers from block copolymer (BCP) precursors has seen a tremendous interest from material scientists because of the possibility to finely tune pore size, functionality, and morphology. Although some feature articles have already been published on this topic,^{4, 6, 7} this up-to-date review addresses the design, synthesis, characterization, and a large overview of some applications of a large number of not only diblock copolymer-based nanoporous materials but also triblock copolymer-derivatized ones.

This review will focus on semi-degradable BCPs that have been so far developed for engineering functional nanoporous polymers. It will first give some general considerations on the synthesis of such nanoporous materials from BCP precursors. A second part will focus on the strategy relying on the degradation of the sacrificial block in diblock copolymers, while the third part will address the selective cleavage of the chemical junction present between the two alien blocks of diblock copolymers. Finally, the last part of this review will be devoted to investigations on triblock copolymers for the preparation of nanoporous frameworks.

2. General Considerations on Functional Nanoporous Polymers Obtained from Diblock Copolymers

2.1. Generalities on diblock copolymer morphologies

Since pioneering studies from Nakahama at the end of the 1980's,⁸ a plethora of examples on the implementation of block copolymers have flourished in the literature. At that time, they prepared symmetric diblock copolymers composed of polyisoprene (PI) and polystyrene (PS) bearing silyl ether group through anionic polymerization from a telechelic polystyrene oligomer. The PI block can be readily removed by ozonolysis, while crosslinking the residual PS block. The methodology based on the implementation of BCPs for the preparation of highly ordered nanoporous polymer frameworks is straightforward and versatile. It first involves a synthetic pathway to afford the desired BCP with narrow molar mass distribution (\mathcal{D}) and controlled volume fraction (f) of the blocks in the macromolecular structure. It is important noticing that the morphology developed by BCPs upon self-organization is governed by three main parameters: (i) the volume fraction of each block, (ii) the length of both blocks (given by N , degree of polymerization), and (iii) the Flory-Huggins interaction parameter between both blocks (χ). Depending on these three parameters, different defined morphologies can be obtained after microphase separation of BCPs, namely alternating lamellae, body-centered spheres, bicontinuous gyroids, close-packed cylinders (**Figure 1a**). Further, the emergence of controlled radical polymerization methods, such as nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) or reversible activation-fragmentation chain-transfer (RAFT) polymerization has brought an ever-growing interest from the polymer scientists to design more and more complex, smart, and advanced materials that can find applications in high-added value technologies. Different studies confronting theoretical studies on the phase diagram morphology of block copolymers and experimental results have been reported in the literature. Bates and Frederikson notably developed experimental phase diagrams of polystyrene-*block*-polyisoprene (PS-*b*-PI) diblock copolymers, as depicted in

Figure 1c.⁹ In the same way, Russell's and Hillmyer's groups contributed a lot to this research by carefully exploring miscellaneous BCP systems.¹⁰⁻¹²

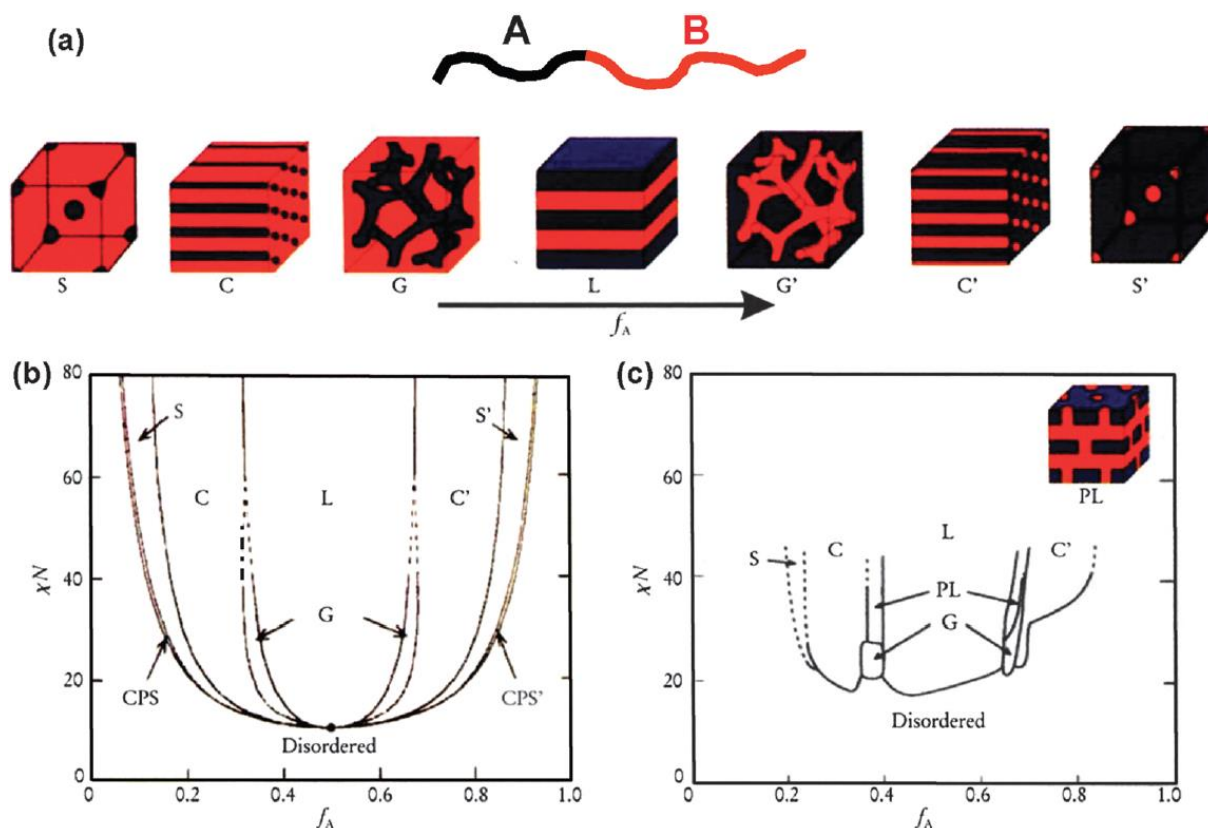


Figure 1. (a) Schematic representations of the defined morphologies expected from microphase separated AB diblock copolymers depending on the volume fraction (f_A) of A block. (b) Theoretical phase diagram expected for AB diblock copolymers depending on f_A and χN . (c) Phase diagram experimentally obtained for PS-*b*-PI diblock copolymers. Reproduced from F. S. Bates, G. H. Fredrickson; Block Copolymers — Designer Soft Materials. *Physics Today* **1999**, 52 (2), 32–38, with the permission of the American Institute of Physics.⁹

While SEM and AFM techniques have been classically used to get some interesting information about the surface morphology of the membranes obtained after etching of the sacrificial block from oriented diblock copolymers, small-angle X-ray scattering (SAXS)¹³ and grazing incidence SAXS (GISAXS)^{14, 15} characterization methods have permitted to give a deeper insight into their fine nanostructuration and their inside structure, as highlighted on **Figure 2**. Indeed, GISAXS has been shown to be a very effective tool to examine the state of orientation of the microdomains in the films, especially during the course of solvent evaporation.¹⁴ Some interesting data on both techniques can be found in well-documented reviews in the field.¹⁶⁻¹⁸

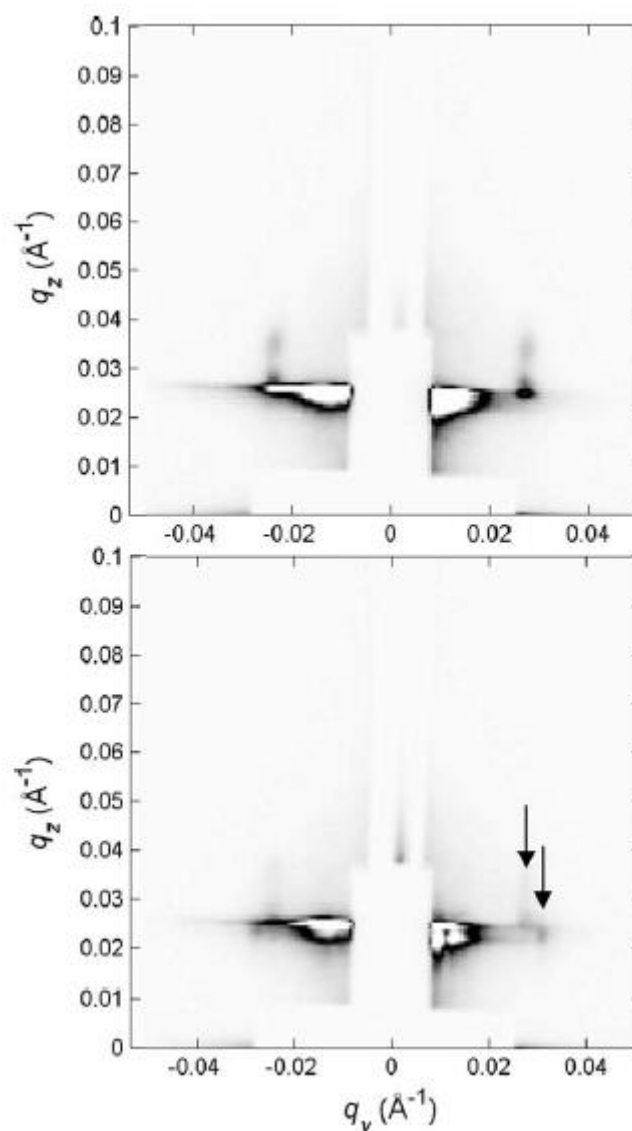


Figure 2. GISAXS patterns at $\alpha = 0.2^\circ$ of PI-*b*-PLA 16-6 diblock copolymer swollen to (a) 30 vol.% and (b) 38 vol.% chloroform. The arrows indicate the position of the reflections arising from parallel cylinders (smaller q_y) and perpendicular cylinders (larger q_y). Reprinted from *Polymer*, 46 (25), Cavicchi, K. A.; Berthiaume, K. J.; Russell, T. P., Solvent annealing thin films of poly(isoprene-*b*-lactide), 11635-11639, Copyright 2005, with permission from Elsevier.

2.2. Orientation of diblock copolymers

Two main strategies have been hitherto implemented for the orientation of domains within BCPs. The first one relies on the alignment of the microstructure of diblock BCPs *via* the shear flow induced by a channel die processing to afford highly oriented structures.¹⁹⁻²¹ The second one is based on the initial casting of a diblock BCP solution onto a suitable substrate to form a thin film, followed by thermal or solvent vapor annealing to reduce defects and improve pattern ordering in the self-organized structure.²²⁻²⁵ The reader should bear in mind that the final porous

morphology (cylinders, gyroids, etc.) of the polymer obtained after degradation of the expendable segment mainly depends on the volume fraction of each block in the BCP precursor. Still, it is worth mentioning that the synthesis of diblock BCPs with rather low dispersity indices (typically with \bar{D} lower than 1.2) seems crucial for each block constituting the copolymer to target the desired morphology.²⁶⁻²⁸ Optimization of the self-organization process is always required in order to improve microphase separation and microdomain orientation when preparing porous polymers from BCP precursors. In this regard, the nature of the solvent used for casting, annealing conditions, and shear alignment, should be carefully taken into consideration. Alternatively, Laus and coworkers demonstrated that the self-organization of PS-*b*-PMMA diblock copolymers can be achieved in 900 s and with long range order through rapid thermal annealing (RTP) of the thin film just by playing with the annealing temperature.²⁹ The authors notably demonstrated that a broad range of copolymers with molar masses from 29.4 to 205 kg.mol⁻¹ could be oriented in this way. Pore diameters d in the 12 to 30 nm range and pore-to-pore distances L_0 ranging from 24 to 73 nm were observed by SEM and GISAXS analysis of the etched thin films.

3. Generalities on removal of sacrificial block and further pore surface functionalization

Once the diblock copolymers orientated, two different strategies exist to remove the sacrificial block from the supramolecular assemblies. The first one, depicted in **Figure 3a**, relies on the chemical degradation of the sacrificial block and generally necessitates harsh reaction conditions to be implemented, which can be detrimental to the orientation of the materials and to the chemical stability of the remaining block. The other smarter strategy to remove the sacrificial block from nanostructured BCPs, more recently developed and depicted in **Figure 3b**, is based on the selective cleavage of the chemical junction present between alien blocks. The etching process should be as mild as possible regarding the polymeric frameworks as it should not alter/destroy the nanostructures arising from the previous nanostructuring step. Careful attention should also be focused onto the mechanical and thermal properties as well as the solvent resistance of the resulting nanoporous frameworks as they should be stable enough to keep their original structure. Well-defined porous morphologies with pore diameters ranging from 10 to 100nm are typically produced.

Once the sacrificial block removed in such self-organized BCPs, chemical functions can be present and thus available at the pore surface for further post-functionalization, depending on the targeted application. To the best of our knowledge, Hillmyer's research group pioneered the functionalization of nanoporous frameworks from BCPs, *i.e.* arising from polystyrene-*block*-

poly(*N,N*-dimethylacrylamide)-*block*-poly(D,L-lactide) (PS-*b*-PDMA-*b*-PLA).³⁰ Upon microphase separation and alignment of the nanodomains, the PLA was etched in 0.5 M NaOH solution. Then, the authors took advantage of the presence of the central PDMA block for functionalizing the pore surface. To this purpose, *N,N*-dimethylacrylamide moieties at the pore surface arising from PDMA were hydrolyzed in 6 M HCl at 80 °C. The released carboxylic acid functions could be in turn reacted with different amines in the presence of a coupling agent (1-hydroxybenzotriazole (HOBt)) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC). Even though the functionalization of these nanoporous frameworks with different amines bearing different functional groups (including alkene, chiral alcohol, or pyridine) rendered them more hydrophilic and could find applications in the nanofiltration research area, such chemical modification of the pore surface is rather time consuming and is processed in harsh reaction conditions. Alternatively, the strategy to produce nanoporous polymeric frameworks from BCPs presenting a selectively cleavable junction allows for the presence of a broad variety of chemical functions at the pore surface and thus for easy access to a broad range of functionalization in milder experimental conditions. Carboxy-decorated nanochannels of porous PS frameworks have been functionalized with amino-containing molecules through the formation of a covalent amide bond in the presence of HOBt/EDC^{19, 20} or EDC/sulfo-*N*-hydroxysuccinimide (*N*-HSS)³¹ as catalytic coupling agents, respectively. Other investigations from Weidman et al.³² and Zhang et al.³³ expanded the scope of this strategy for the efficient immobilization of ligands, such as glutathione (GSH), cysteamine, and 2-aminoethane-1,1-disulfonic acid.

Sulfonic acid functions positioned at the pore surface of nanoporous PS were also successfully transformed into the corresponding sulfonamide by reaction with an amine-containing chemical compound after preliminary activation of the sulfonyl functionality in the presence of thionyl chloride.³⁴ A smart strategy to generate hydrophilic pores from sulfhydryl decorated nanopores from PS materials was developed by Le Droumaguet *et al.*³⁵ Experimentally, mild radical thiol-ene addition of allyl-appended PEO was adopted for functionalizing sulfhydryl moieties lining the surface of cylindrical pores. Even though an unsatisfactory 50% grafting yield was obtained, likely due to steric hindrance, the authors claimed that this work paved the way towards easy and straightforward derivatization of the pore surface with hydrophilic or hydrophobic macro(molecules), giving rise to a plethora of pore surface chemical composition depending on the targeted application. In this case, the grafting of PEO chains at the pore surface allowed for increasing the wettability of the nanoporous frameworks and thus crossing of water molecules through the nanopores.

Inorganic particles, such as nanometals, have been also successfully immobilized at the pore surface of nanoporous polymers through the establishment of covalent-like Au-S bonds. It was notably demonstrated by Ryu *et al.*³⁶ and our group.^{35, 37} This functionalization with metallic nanoparticles could lead to the preparation of advanced hybrid materials that could serve as nanoreactors in supported heterogeneous catalysis, such as nitroarene reduction. Poupart *et al.* took advantage of the presence of aldehyde at the pore surface to graft a series of amine, such as tetraethylene pentamine (TEPA), through reductive amination.³⁴ The resulting grafted amine groups were in turn implemented for the adsorption of Au³⁺ and further gold nanoparticles after NaBH₄-mediated reduction of gold cations.

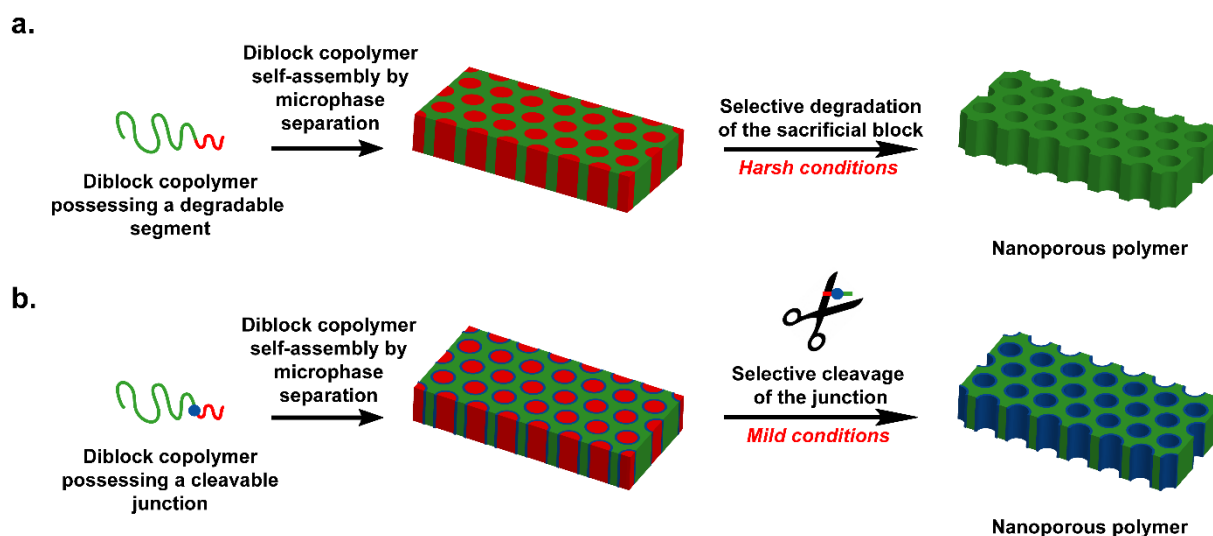


Figure 3. Schematic representation of the two main synthetic pathways for the preparation of nanoporous polymers *via* (a) etching of the sacrificial block and (b) selective cleavage of the chemical junction between both blocks.

4. Nanoporous Polymers Derived from Semi-Degradable Diblock Copolymers via Etching of Sacrificial Block

Table 1 gathers the main experimental etching conditions required for the removal of sacrificial block from semi-degradable diblock copolymers. They are mainly dictated by the nature of the sacrificial block but also by that of the residual block. For instance, basic or acidic hydrolysis of the ester bonds present in the PLA backbone in hydro-alcoholic solutions remains the strategy of choice to remove such sacrificial block from PS-*b*-PLA diblock copolymers to produce nanoporous polystyrene.^{10, 11, 19, 20, 38} In this case, PS is always the remaining block as it has a strong chemical stability towards such harsh degradation conditions. An alternative was reported by Sarkar and Stefik that recently demonstrated the possibility to degrade the PLA block in PLA-*b*-PS BCPs in less aggressive experimental conditions, *i.e.* through trifluoroacetic acid (TFA)-mediated acidic hydrolysis³⁹. Alternatively, iodhydric acid-based hydrolysis has

been implemented for the degradation of poly(ethylene oxide) (PEO) in PS-*b*-PEO diblock copolymers ⁴⁰.

UV treatment followed by acetic acid extraction or γ irradiation exposure were generally implemented for the degradation of poly(methyl methacrylate) (PMMA) block in PS-*b*-PMMA ^{31, 41, 42}, PFS-*b*-PMMA ⁴³, poly(4-bromostyrene) (PBrS)-*b*-PMMA ¹², or 1,2-PB-*b*-PMMA diblock copolymers ⁴⁴. Fluorine-based chemicals, such as TBAF or HF, allowed for the degradation of poly(dimethyl siloxane) (PDMS) in PI-*b*-PDMS, ⁴⁵⁻⁴⁷ PS-*b*-PDMS^{48, 49} or PB-*b*-PDMS⁵⁰ (see **Figure 4** for gyroid-type morphology obtained from such diblock copolymers) diblock copolymers. Poly(propylene glycol) (PPG) blocks present in PIM-*b*-PPG were generally degraded by oxygen plasma treatment or in the presence of fuming nitric acid ⁵¹. Finally, etching of polyisoprene (PI) in PS-*b*-PI diblock copolymers could be achieved by ozonolysis, as mentioned above. ^{8, 52} In the last years, Coulembier's research group also developed poly(3-hexylthiophene)-*block*-poly(phthalaldehyde) (P3HT-*b*-PPA) copolymers whose sacrificial PPA block could be depolymerized by thermal treatment at 110 °C for short period of time (30 min).⁵³

Table 1. Experimental conditions employed for the selective removal of the sacrificial block from BCP precursors.

Nature of the sacrificial block	Associated block copolymer	Degradation conditions	Porous morphology	References
PLA	PS- <i>b</i> -PLA	Basic or acidic hydrolysis	Cylinders, gyroids, lamellae	10, 11, 19, 20
PEO	PS- <i>b</i> -PEO	Reaction with HI	Cylinders	39
PMMA	PB- <i>b</i> -PMMA, PS- <i>b</i> -PMMA, PFS- <i>b</i> -PMMA, (PBrS)- <i>b</i> -PMMA and 1,2-PB- <i>b</i> -PMMA	UV treatment followed by acetic acid extraction or γ irradiation exposure	Cylinders	12, 41-44
PDMS	PI- <i>b</i> -PDMS and PS- <i>b</i> -PDMS	Reaction with TBAF or HF	Cylinders gyroids	40, 49
PPG	PIM- <i>b</i> -PPG	Oxygen plasma treatment or degradation with fuming nitric acid	Not investigated	51
PI	PS- <i>b</i> -PI	Ozonolysis	Cylinders, lamellae, spheres, bicontinuous	8, 52

PPA	P3HT- <i>b</i> -PPA	Thermal treatment	Fibrils	53
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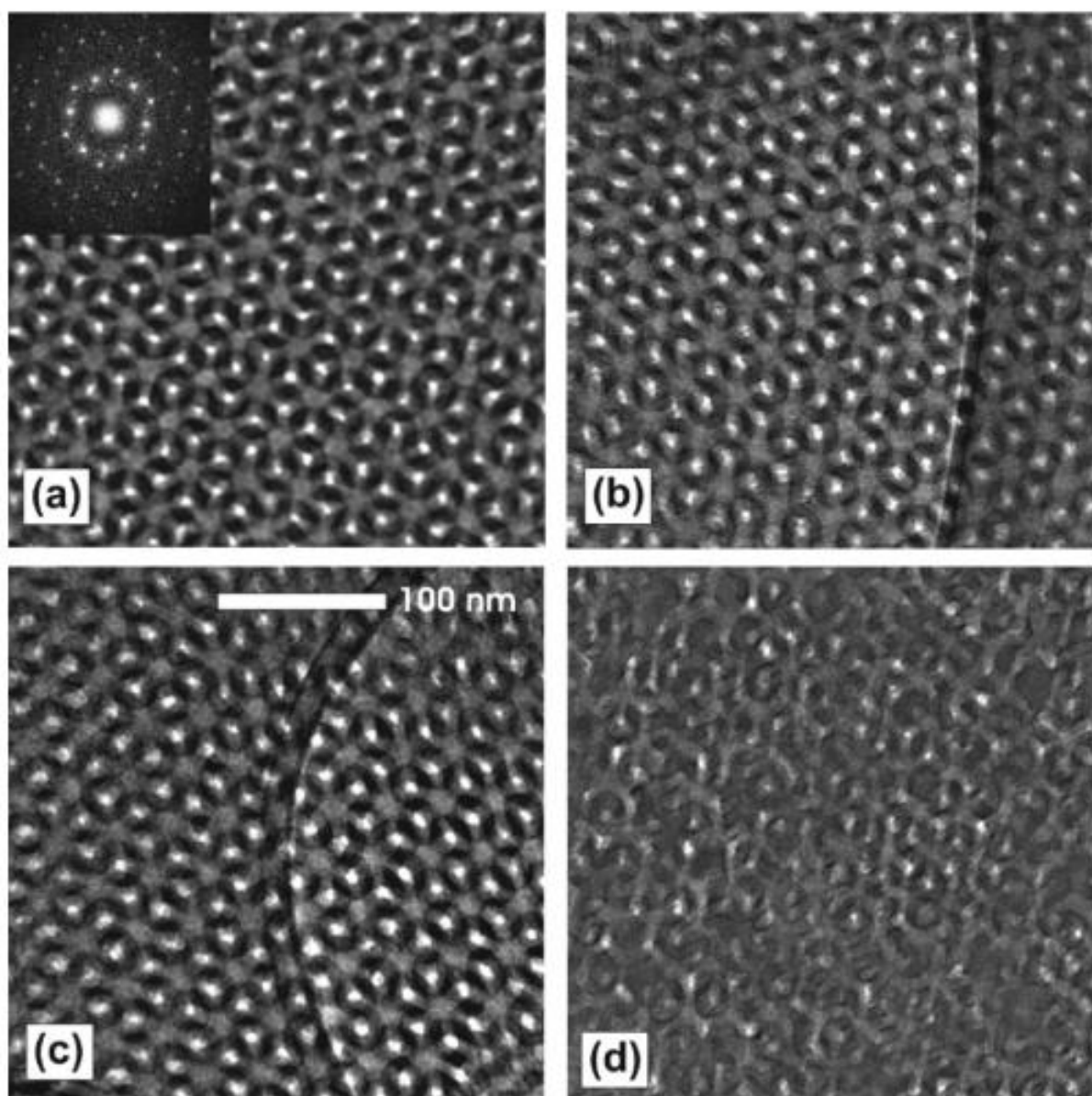


Figure 4. SEM micrographs of nanoporous PB arising from PB-*b*-PDMS BCP presenting a gyroid morphology after cross-linking of PB at 140 °C for 2 h under argon and subsequent PDMS etching in the presence of tetrabutylammonium fluoride. Samples are taken at (a) 0, (b) 10, (c) 30, and (d) 40 h of UV treatment, respectively, to photo-oxidize eventually remaining double bond of the PB nanoporous material. Reprinted with permission from ref. ⁵⁰ Copyright 2016 American Chemical Society.

5. Nanoporous Polymers Derived from Diblock Copolymers by Selective Cleavage of Junction Positioned Between Both Blocks

The design of block copolymers from small molecules (initiators, transfer agents) possessing labile chemical bonds within their structure constitutes an elegant means to engineer functional

nanoporous materials by cleaving the latter bonds in precise and selective conditions in order to release the sacrificial block when needed. This strategy possesses different advantages over the previous approach. It allows for the removal of the sacrificial block to be proceeded in rather mild experimental conditions that would not be detrimental to the nanostructure or to the chemical stability of the remaining polymer. Additionally, the selective cleavage of the junction also allows for the direct release of chemical functionalities that will decorate the nanopore surface. Such examples of selective cleavage of the chemical junction present between both blocks have flourished in recent literature.

5.1. Cleavage through a photo-triggered mechanism

Goldbach *et al.*^{54, 55} were the pioneers on implementing such a strategy based on the selective cleavage of the chemical junction present between both blocks (**Figure 5a**). In their investigations, they developed anthracene end-functionalized homopolymers that were coupled through a photo-triggered cycloaddition reaction between anthracene moieties. Experimentally, the polymerization of styrene block by anionic polymerization using BuLi as the initiator was quenched with 2-(bromomethyl)anthracene, thus providing an anthracene-end-capped homopolymer. In parallel, PMMA was prepared from anionic polymerization initiated from an anion produced *in situ* by reaction of BuLi on 1-phenyl-1-(2-anthryl)ethylene. The resulting block copolymer was obtained from reaction of anthracene end-capped homopolymers under UV irradiation at 330 nm. Upon spin coating of the resulting PS-*b*-PMMA copolymer solution on silicon wafers and thermal heating at 170 °C under vacuum, thus allowing for the selective cleavage of the anthracene photo-dimer junction. Eventually, this selective cleavage was also possible under UV irradiation at 280 nm to obtain nanoporous polystyrene.

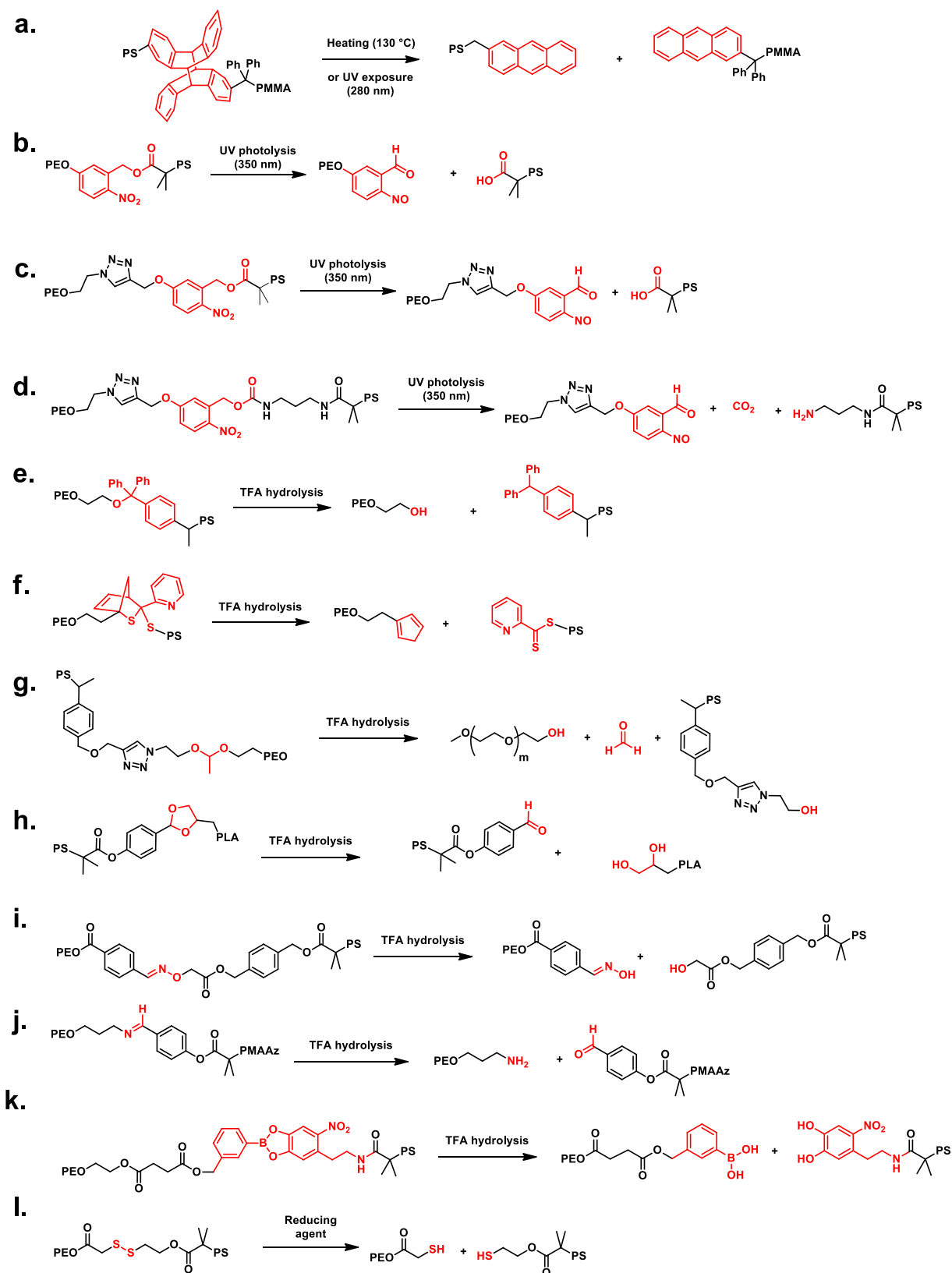


Figure 5. Experimental conditions required for the selective cleavage of functional chemical junctions present between incompatible segments in diblock copolymers. (a-d) phototriggered degradation of the junction, (a-k) acidic hydrolysis, and (l) under reducing conditions.

Ortho-nitrobenzyl (ONB) groups have also been positioned at the junction between alien blocks of PEO-*b*-PS diblock copolymers, as depicted on **Figure 5b**.⁵⁶ Experimentally, a ONB-containing PEO ATRP macroinitiator was prepared through a three-step synthetic strategy. First, aldehyde function from commercial 5-hydroxy-2-nitrobenzaldehyde was reduced with NaBH₄ to afford the corresponding primary alcohol. The phenol proton was abstracted by reaction with NaH and the as-formed phenolate was allowed to operate the nucleophilic substitution of α -methoxy- ω -tosyl-appended PEO. A final reaction was necessary to proceed the esterification of the available primary alcohol by α -bromoisobutyryl bromide. Then, the polymerization of styrene was successfully achieved from the prepared ATRP macroinitiator to obtain diblock copolymers with low D (<1.15) and fine control of the molecular structure of the copolymer. Exposition of thin films formed from those diblock PS-*b*-PEO copolymers to UV light at 350 nm demonstrated the selective cleavage of the ONB junction and allowed for the generation of the nanoporous structure of the films. Later, Ma *et al.*⁵⁷ developed the same synthetic strategy based on a ONB junction to produce diblock copolymers constituted of a hydrophilic PEO segment and a hydrophobic block containing styrene and coumarin-functionalized styrene (**Figure 5c**). Experimentally, the authors prepared a PEO-based ONB-containing ATRP macroinitiator through a synthetic strategy notably involving CuAAC “click” chemistry reaction to couple PEG to the ONB-containing ATRP initiator. The latter was used for the polymerization of styrene and a coumarin-functionalized styrene. The resulting thin films from these novel diblock copolymers could be etched by selective cleavage of the ONB junction under UV exposure at 365 nm. More interestingly, not only this strategy permitted to expose carboxyl functions at the pore surface, but it also allowed for a crosslinking of the resulting nanoporous PS through dimerization of pending coumarin groups of the polystyrene block.

Gohy’s research group expanded the field of this chemical junction to prepare PS-*b*-PEO diblock copolymers containing a ONB junction connected to a carbamate. To this purpose, 3-hydroxymethyl-4-nitrophenol was reacted with propargyl bromide after deprotonation with potassium carbonate.⁵⁸ The resulting intermediate was activated with carboxydiimidazole (CDI) and coupled with 1,3-diaminopropane that was finally reacted with α -bromoisobutyryl bromide to afford the resulting ATRP initiator. The diblock copolymer was prepared in one-pot by achieving the ATRP polymerization of styrene concomitant to the “click” coupling of α -azido- ω -methoxy PEO ($M_n \sim 5000 \text{ g}\cdot\text{mol}^{-1}$). Upon formation of the thin films by spin coating and solvent vapor annealing, the junction between each block was cleaved under UV irradiation at 300 nm, thus giving rise to porous polymeric scaffolds (see **Figure 6**) with cylindrical

nanopores oriented perpendicularly to the substrate surface and functionalized with amine functions (**Figure 5d**).

Theato's research group also implemented this junction for developing nanoporous polymers from diblock copolymers.^{59,60} They notably synthesized PS-*b*-PEO containing a ONB junction *via* two strategies: one approach involving the polymerization of styrene from a PEO-macro-RAFT agent containing the ONB moiety, and another one relying on the post-polymerization “click” CuAAC coupling of a ONB-containing propargyl-terminated PS segment with an azido-appended PEO block. Alternatively, they also prepared poly(pentafluorophenyl (meth)acrylate)-*block*-PEO (PPFP(M)A-*b*-PEO) diblock copolymers possessing this ONB junction. Again, the UV degradation of the ONB chemical junction occurred at 365 nm using a 500 W UV lamp. Eventually, the authors proceeded to the crosslinking of the polymer chains by contact of the resulting nanoporous thin films with a diamine, *e.g.* hexamethylenediamine or cysteamine.

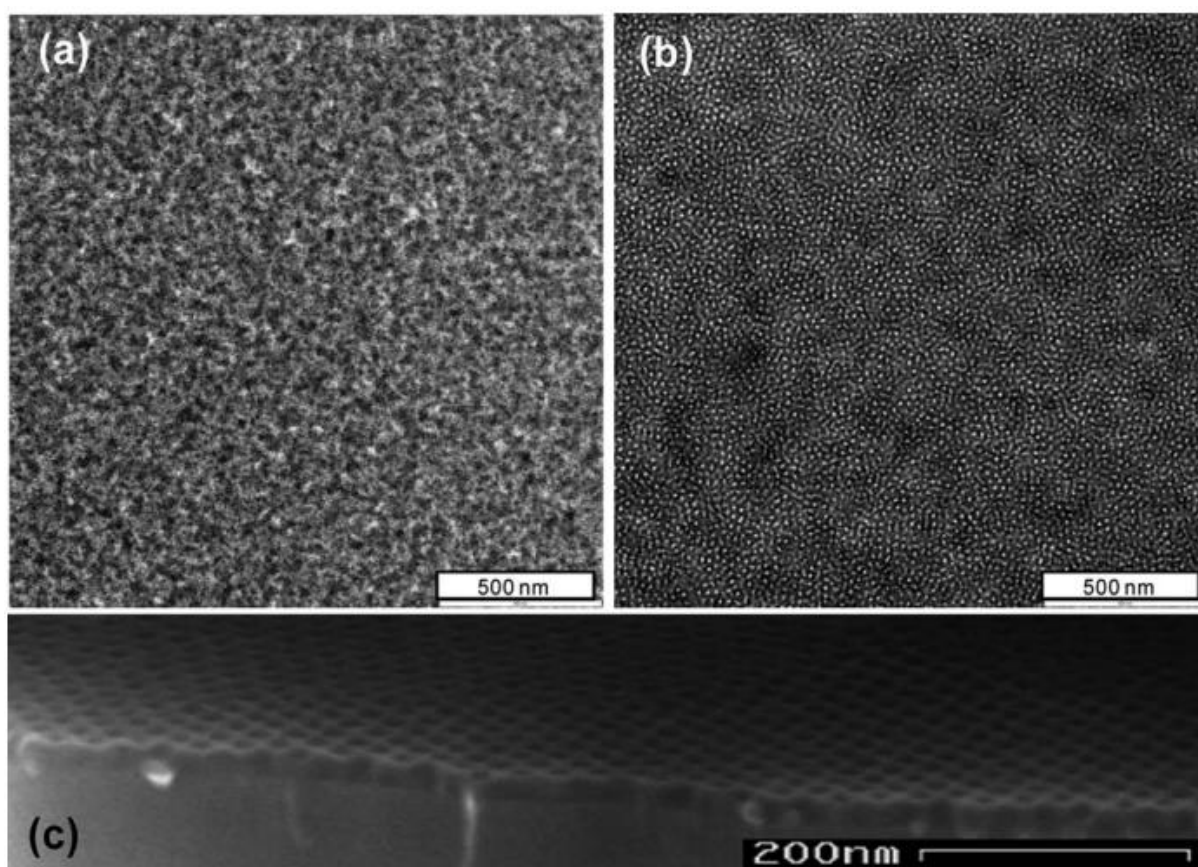


Figure 6. (a) TEM micrograph of PEO₁₁₃-*b*-PS₂₃₀ thin films presenting a ONB junction after solvent vapor annealing in a benzene/water mixture and staining with RuO₄, (b) TEM image of the same annealed film stained with RuO₄ after extraction of the PEO sacrificial block, (c) SEM cross-sectional image of a nanoporous PS₂₃₀ thin film, upon PEO extraction. Reprinted with permission from ref. ⁵⁸ Copyright 2016 American Chemical Society.

5.2. Removal of the sacrificial block under acidic conditions

Trityl ether, sensitive to Lewis and Brønsted acids, has been used by Yurt *et al.* to prepare nanoporous polystyrene (**Figure 5e**).⁶¹ In their study, the co-authors prepared a PEG-TEMPO macroinitiator. Experimentally, they added TEMPO to 4-bromostyrene. Then, the bromide in 4-bromostyrene-TEMPO adduct was converted into its lithium analogue by a lithium-halogen exchange in the presence of *n*-BuLi at -78 °C. The resulting lithiated styrene-TEMPO adduct was added to benzophenone to afford diphenyl[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)phenyl]methanol that was reacted with methanesulfonyl-terminated methoxypoly(ethylene oxide). The as-obtained PEG-TEMPO macroinitiator allowed styrene to be polymerized *via* nitroxide-mediated polymerization at 130 °C. Resulting PEO-*b*-PS copolymers possessed a trityl ether junction with narrow molar mass distribution ($D = 1.18$). The authors demonstrated that PEO could be cleaved in the solid state using TFA vapors. Later, Zhang *et al.* expanded the scope of this particular ligation to prepare highly ordered nanoporous thin films on silicon wafers from PEO-*b*-PS copolymers possessing a trityl ether junction.⁶² After solvent casting and subsequent solvent annealing, the PEO block was removed by selective cleavage in the same condition, *i.e.*, in the presence of TFA.

The use of such trityl ether cleavable junction was also developed in conjunction with ATRP to produce degradable diblock copolymers. Thus, Qi *et al.* prepared PEO-*b*-PMMA copolymers. The synthetic strategy involved the mesylation of methoxy-end capped PEO.⁶³ It was then coupled with the alkoxide formed *in situ* by reaction of 4-vinylphenyl diphenylmethanol with NaH to afford the corresponding vinyl terminated PEO. Hydroboration followed by oxidative cleavage of the intermediate afforded the corresponding alcohol that was esterified with α -bromoisobutyryl bromide. The as-obtained ATRP macroinitiator was used to trigger methyl methacrylate (MMA) polymerization. The resulting nanoporous PMMA could be obtained upon spin coating, subsequent solvent annealing, and final etching of PEO through treatment of the films with TFA vapors for 30 s. The authors notably claimed that such nanoporous materials could find applications in Recessed Nanodisk-array Electrode (RNE) or as a template to fabricate nanoelectrode array for sensor applications.

Glassner *et al.* implemented the retro-Diels-Alder cycloaddition to produce nanoporous PS from PEO-*b*-PS diblock copolymers (**Figure 5f**).⁶⁴ To this purpose, a commercial α -methoxy-PEO was tosylated and the resulting intermediate was reacted with bis(cyclopentadienyl)nickel(II). In parallel, benzylpyridin-2-yl dithioformate transfer agent was used to control the RAFT polymerization of styrene. A final Diels-Alder cycloaddition step between the cyclopentadienyl-appended PEO and the pyridinyl dithioester-terminated PS was

successfully achieved in the presence of TFA at room temperature. The etching of the thin films prepared from these copolymers to obtain the corresponding nanoporous PS was carried out at 90 °C, *i.e.* the temperature that was necessary to proceed the retro-Diels Alder cycloaddition reaction. The presence of available amino groups at the pore surface was revealed by coupling reaction of the free amino groups of the porous PS with coumarin 343.

Acetal junctions have also been the subject of macromolecular engineering investigations to develop PS-*b*-PEO presenting an acid cleavable junction. Hawker's research group prepared some acid cleavable PS-*b*-PEO diblock copolymers through a combination of "click" chemistry and NMP-type controlled radical polymerization (**Figure 5g**).⁶⁵ To this purpose, PEO was reacted with chloro-ethyl vinyl ether (CEVE) in the presence of pyridinium *p*-toluenesulfonate (PPTS) to furnish the corresponding acetal-containing chloro-appended PEO. The chlorine was transformed into an azido group through nucleophilic substitution in the presence of NaN₃ in DMF. The resulting azido-terminated PEO could undergo a "click" 1,3-dipolar Huisgen cycloaddition with a TEMPO adduct of an alkyne-bearing styrene. Final bulk NMP of styrene from this TEMPO-derivatized macroinitiator allowed for the synthesis of diblock copolymers with narrow molar mass distribution ($\mathcal{D} = 1.16$). Later on, Grancharov *et al.*⁶⁶ produced nanoporous P3HT from P3HT-*b*-PEO diblock copolymer precursors presenting an acetal junction using a similar strategy. Methoxy-appended PEO was reacted subsequently with CEVE and PPTS. A final substitution of the terminal chlorine in the presence of NaN₃ allowed for the obtention of a α -methoxy ω -azido PEO that was reacted with ω -hydroxy P3HT obtained by Grignard metathesis and preliminary esterified with pentynoic acid. Exposition of thin films of this copolymer to TFA vapors, followed by dipping into a MeOH/TEA 100/1 (v/v) mixture, allowed for PEO segment removal thanks to acetal cleavage. Another example of such acetal function implemented at the junction of diblock copolymers was reported by Poupart *et al.*³⁷ (**Figure 5h**) In their investigations, a heterobifunctional initiator was obtained through a two-step synthetic path in which *para*-hydroxybenzaldehyde was first acetalized with glycerol in the presence of APTS to afford the resulting 5-membered ring acetal intermediate that was in turn reacted with α -bromoisobutyryl bromide. The resulting heterobifunctional initiator was used to initiate consecutively the ring-opening polymerization (ROP) of D,L-lactide and the controlled ATRP of styrene. In this case, the junction present in the resulting films of PS-*b*-PLA diblock copolymers could be selectively cleaved in the presence of TFA in EtOH.

Alternatively, another acid cleavable chemical junction, *i.e.* oxy-imine, could be inserted at the junction between sacrificial and remaining blocks of BCPs (**Figure 5i**). Rao *et al* indeed proposed the synthesis of an ATRP macroinitiator containing this particular moiety.⁶⁷

Experimentally, the authors proceeded to the monoesterification of *para*-xylene glycol with α -bromoisobutyryl bromide. The resulting ATRP initiator was once again esterified with 2- (tert-butyloxycarbonylaminoxy)acetic acid. After Boc deprotection of the resulting intermediate upon TFA treatment in DCM, oxy-amine-appended ATRP initiator was obtained and directly coupled with aldehyde-terminated PEO. The as-obtained oxy-imine macroinitiator allowed for the successful ATRP of styrene. After thin film formation through spin-coating and subsequent solvent annealing, the resulting phase-separated copolymer films were immersed in a TFA solution and transferred to a water bath to allow for solubilizing the PEO block.

Li *et al.* implemented the use of imine function at the junction of a diblock copolymer named PEO-*b*-PMAAz, PMAAz consisting of a methacrylate block bearing azobenzene side chains (**Figure 5j**).⁶⁸ To this purpose, PEO amine was reacted with *para*-hydroxybenzaldehyde to produce the resulting imine-containing hydrophilic block. A subsequent step consisting of the esterification of this intermediate compound with α -bromoisobutyryl bromide allowed for the synthesis of the resulting PEO-based ATRP macroinitiator. It was used to initiate the polymerization of azobenzene-bearing methacrylate, and then provide the PEO-*b*-PMAAz copolymer with $D = 1.2$. In this case, HCl aqueous solution treatment of thin films, followed by their washing with MeOH, afforded PMAAz nanoporous films.

Bakangura *et al.*⁶⁹ developed an elegant strategy to prepare nanoporous polystyrene from PS-*b*-PEO multi-stimuli responsive diblock copolymers containing an original boronate junction. The strategy used a convergent synthesis in which the two PS and PEO blocks were independently engineered to bear either a catechol or a phenylboronic acid end-group, as depicted in **Figure 7**. The last step of this synthetic path involved the coupling of the two homopolymers through boronate ester formation. Upon spin coating of the copolymer solubilized in THF on silicon wafers, subsequent orientation through solvent casting, and final removal of the PEO block through selective cleavage of the boronate junction using a TFA solution (**Figure 5k**), nanoporous PS thin films displaying a cylindrical morphology were obtained. The presence of boronic acid or catechol functions at the pore surface could be envisioned for applications related to heterogeneous supported catalysis or sugar capture.

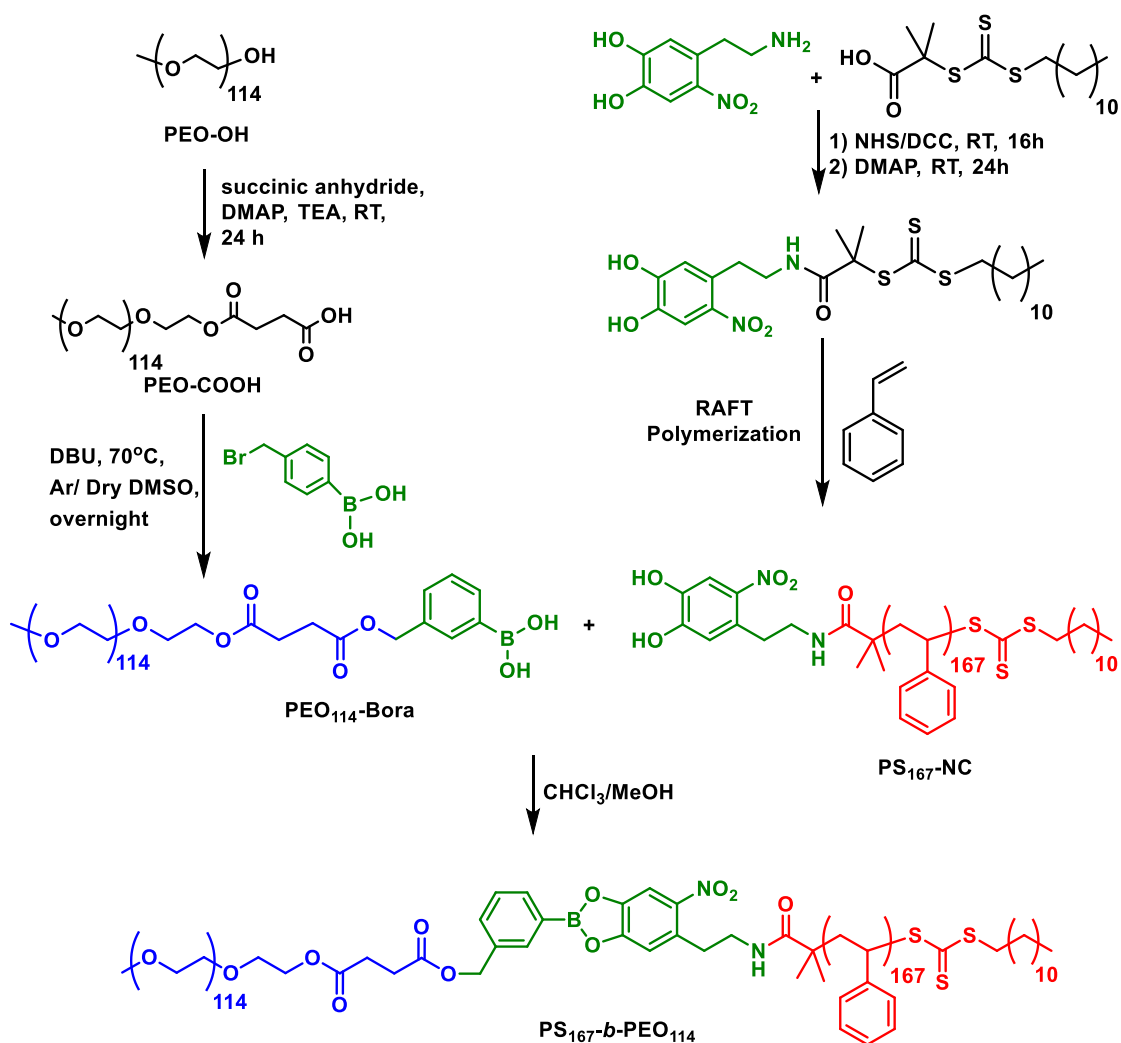


Figure 7. Synthetic pathway adopted for the preparation of PS-*b*-PEO diblock copolymers containing a selectively cleavable boronate junction. Reprinted with permission from ref. ⁶⁹ Copyright 2022 Royal Society of Chemistry.

5.3. Reducing conditions for selective cleavage of the junction

Ryu *et al.* successfully demonstrated that disulfide bridges can be inserted within the structure of block copolymers (**Figure 5l**).³⁶ Experimentally, the authors prepared a macro-RAFT agent *via* a two-step synthetic procedure involving the esterification of monomethoxy-appended PEO by thioacetic acid in the presence of PTSA and the subsequent reaction of the thiol-terminated PEO with a RAFT agent presenting a pyridyl disulfide moiety to afford the resulting macro-RAFT agent containing a disulfide bridge. It was used to polymerize styrene through RAFT-mediated controlled radical polymerization. Nanoporous polystyrene could be obtained from this BCP by spin coating of the PS-*b*-PEO, solvent vapor annealing using a benzene/water mixture, and selective cleavage of the disulfide juncture by reaction with a reducing agent, *i.e.*

DTT. The presence of thiol functions at the surface of the as-obtained cylindrical nanopores was evidenced.

More recently, Le Droumaguet *et al.* implemented a similar strategy for producing nanoporous PS from PLA-*b*-PS diblock copolymer containing the same junction between both blocks.³⁵ To this purpose, the authors proposed the mono-esterification of bis(2-hydroxyethyl) disulfide with α -bromoisobutyryl bromide to afford a heterobifunctional initiator, *i.e.* 2-[(2-hydroxyethyl)dithio]ethyl 2-bromoisobutyrate that was used to initiate successively ring-opening polymerization of D,L-lactide in the presence of tin(II) 2-ethylhexanoate, and Atom Transfer Radical Polymerization of styrene in the presence of the Cu(I)Br/PMDETA system. The resulting copolymers were oriented through channel die processing, and the sacrificial PLA block was removed through selective cleavage of the disulfide bridge in the presence of a solution containing triphenylphosphine as the reducing agent solubilized in MeOH. In such a way, nanopores in the 10 nm diameter range were thus obtained, as observed in **Figure 8**. The authors took advantage of the presence of thiol functions at the pore surface to immobilize gold nanoparticles through covalent-like Au-S bonds or to graft PEO chains at the pore surface through “click” thiol-ene radical addition with an allyl PEG derivative.

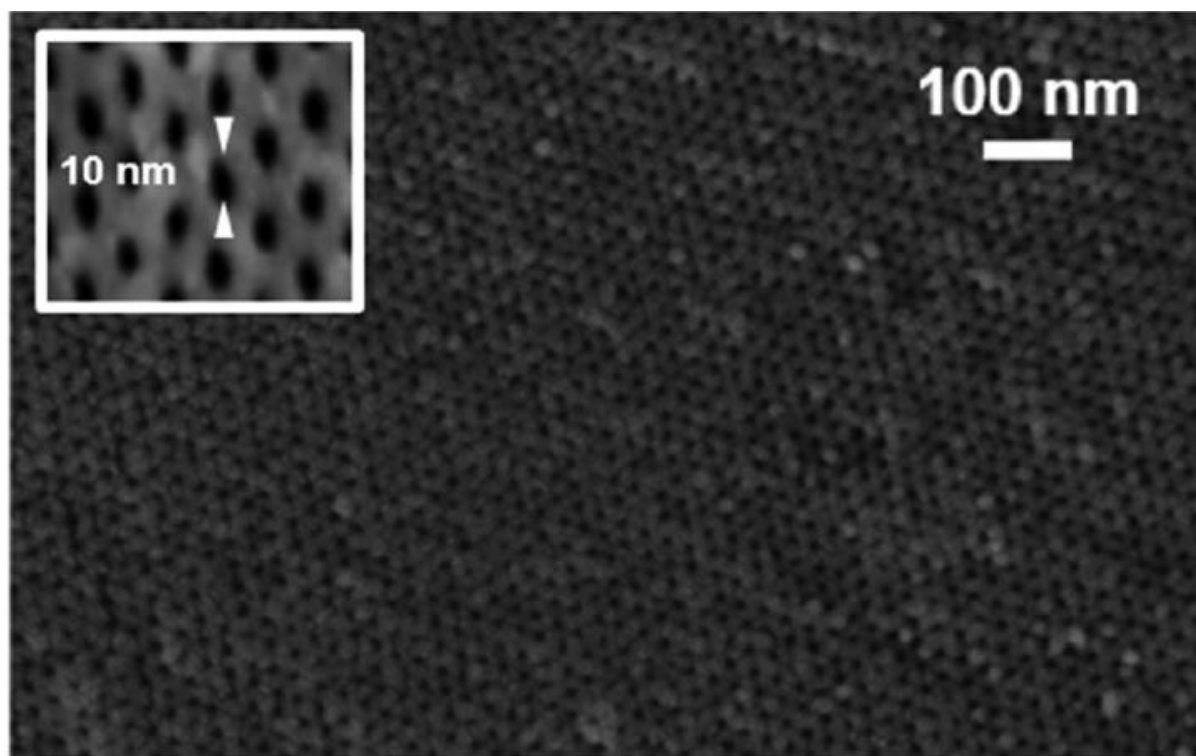


Figure 8. SEM picture of a cross-section of a channel die-oriented parallelepiped of PS₁₀₄-*b*-PLA₅₉ diblock copolymer upon removal of the PLA sacrificial block by selective PPh₃-mediated cleavage of the disulfide junction. Inset: zoom of the nanopore array ($D_p = 10$ nm). Reprinted with permission from ref. ³⁵ Copyright 2015 Royal Society of Chemistry.

5.4. Selective cleavage of non-covalent interactions

More exotic non-covalent junctions have also been elegantly implemented for the preparation of nanoporous polymers from the corresponding diblock precursors. For instance, the selective cleavage of a ruthenium (II)-terpyridine bis-complex positioned at the junction between PEO and PS macromolecular components of the corresponding diblock copolymers has been highlighted by Fustin *et al.*⁷⁰ Both blocks were capped with terpyridine moieties, and their coupling was achieved in the presence of ruthenium trichloride (RuCl_3) in MeOH at 60 °C for 24 h. Upon orientation of the “pseudo” BCP, nanoporous PS films could be obtained by simple oxidation of Ru (II) to Ru (III) by immersion in a $\text{Ce}(\text{SO}_4)_2$ aqueous solution brought to pH 1 that allowed for the selective cleavage of the junction (**Figure 9a**). More recently, Mugemana *et al.*⁷¹ expanded the scope of this synthetic strategy, simply by changing the nature of the metal used to create a non-covalent bis-complex between sacrificial and remaining blocks, *i.e.* nickel (II). In this particular case, the metal-terpyridine complex was cleaved by immersing the thin films in KCN aqueous solution to remove the PEO sacrificial block, as shown in **Figure 9b**.

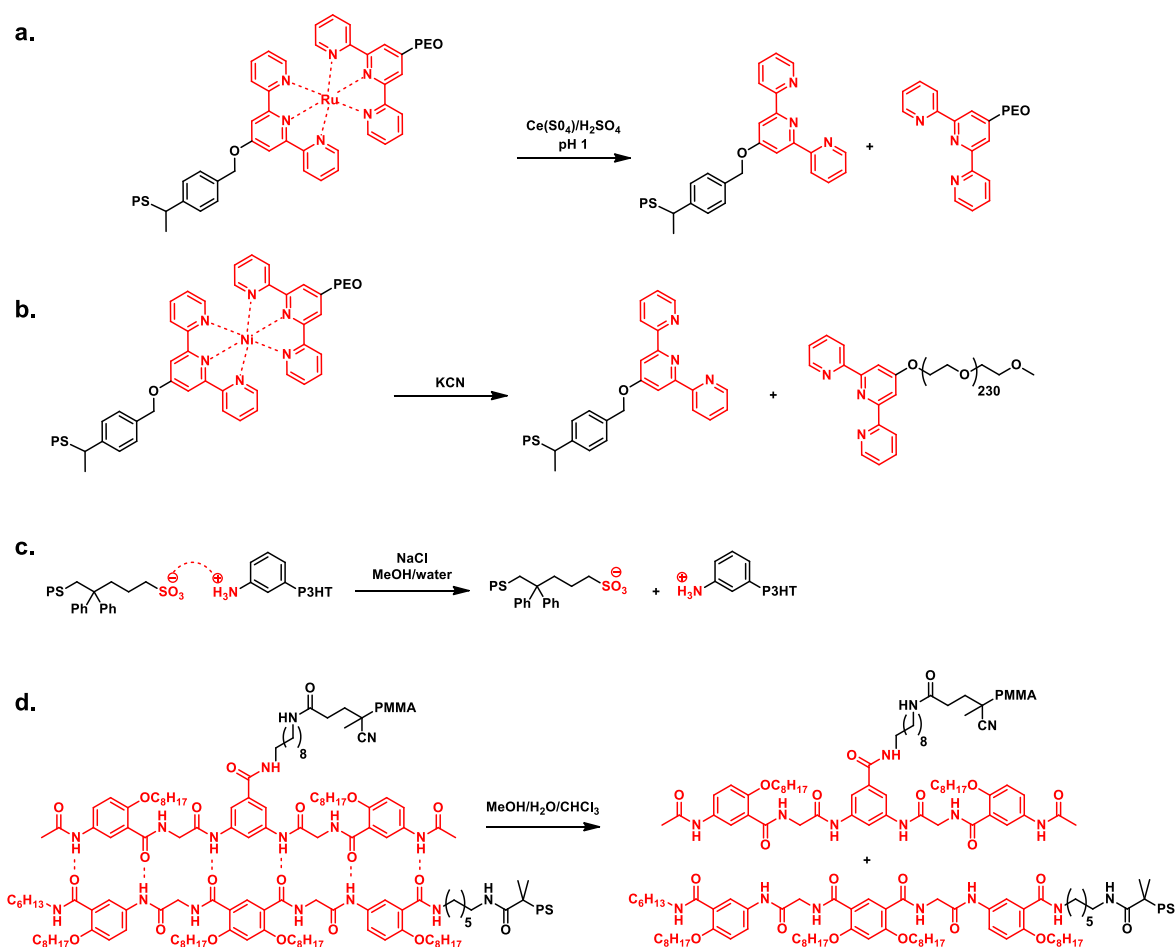


Figure 9. Experimental conditions utilized for the selective cleavage of non-covalent junctions positioned between alien blocks in diblock copolymers. (a-b) coordination breaking, (c) electrostatic interaction breaking and (d) hydrogen bond breaking.

The formation of ionic pairs between sulfonate ($-\text{SO}_3^-$) and ammonium ($-\text{NH}_3^+$) termini of distinct polymer segments has also been implemented by Takahashi *et al.* for generating “pseudo” BCP, and the corresponding nanoporous materials after cleavage of the ionic bonds existing between both blocks.⁷² To this purpose, a poly(3-hexylthiophene) (P3HT) was prepared by anionic polymerization initiated by [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) ($\text{Ni}(\text{dppp})\text{Cl}_2$) species. The polymerization was quenched with 3-[bis-(trimethylsilyl)amino]phenylmagnesium chloride which allowed to obtain an amine capping after removal of the trimethylsilyl protecting groups in 5 M HCl. In parallel, a polystyrene block was produced by anionic polymerization from *sec*-BuLi. After appropriate conversion of styrene, 1,1-diphenylethylene (DPE) and 1,3-propane sulfone were sequentially added to the polymerization mixture, which afforded a sulfonic acid-appended PS. The formation of the “pseudo” BCP was achieved by slowly evaporating a solution of equimolar amount of P3HT-NH₂ and PS-SO₃H blocks dissolved in toluene. The thin films were solvent annealed in a chamber exposed with toluene steam for 3 h, and the nanoporous P3HT was obtained after soaking of the latter in a EtOAc/TEA 100/1 (v/v) solution (**Figure 9c**).

Hawker and Drockenmuller collaborated on the development of “pseudo” BCP structures presenting a non-covalent supramolecular junction based on hydrogen bonding.⁷³ This elegant strategy relied on the preparation of sacrificial and remaining blocks presenting complementary donor-acceptor hydrogen-bonding structures building blocks, *i.e.* a symmetrical oligoamide (SOA) and an asymmetrical oligoamide (AOA) terminus, respectively. Experimentally, one macro-RAFT agent presenting the SOA structure allowed for the production of the PMMA block, while the other macro-RAFT agent presenting the OAO structure was used for the polymerization of styrene. PMMA block etching was achieved in very mild conditions as hydrogen bonds can be broken rather easily by playing with the solvent nature. To this purpose, the hydrogen bond breaking of the complementary oligoamide moieties between both blocks occurred in a MeOH/H₂O/CHCl₃ solvent mixture (**Figure 9d**).

6. Nanoporous Materials Derived from Functional Triblock Copolymers

6.1. General considerations on triblock copolymers

Multiblock copolymers, and especially triblock copolymers, possessing or not an expendable block have been prepared and successfully used as precursors for the preparation of a broad range of functional nanoporous materials with pore sizes in the nanoscopic range (10–65 nm). These original studies have notably relied on ABC asymmetric triblock copolymers, *e.g.* PS-*b*-

PMMA-*b*-PEO,⁷⁴ PS-*b*-PDMA-*b*-PLA,³⁰ PS-*b*-PI-*b*-PLA,⁷⁵ PDMS-*b*-PtBA-*b*-PS,⁷⁶ PB-*b*-P2VP-*b*-PtBA,⁷⁷ and PS-*b*-P2VP-*b*-PtBA,⁷⁷ PS-*b*-PMMA-*b*-PtBA (see **Figure 10** for images of corresponding porous morphology),⁷⁸ among many others.

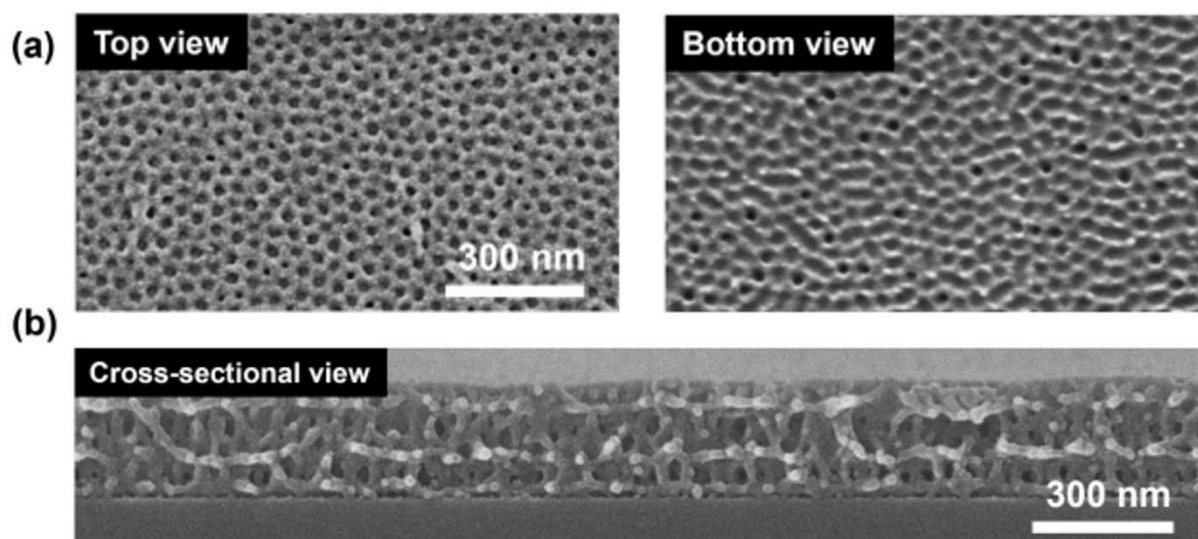


Figure 10. (a) Top and (b) bottom SEM images of a 200-nm thick PS-*b*-PMMA-*b*-PtBA film. The film was prepared directly onto a substrate modified with a random copolymer composed of styrene and MMA (for neutrality), then the BCP films were subjected to thermal annealing at 170 °C for 48 h under vacuum. (c) Cross-sectional SEM image of the same BCP film. Reprinted with permission from ref. ⁷⁸ Copyright 2019 American Chemical Society.

On the other hand, some investigations have also reported on ABA symmetric triblock copolymers, such as PLA-*b*-PS-*b*-PLA⁷⁹ and polyisoprene-*block*-poly(pentamethyldisilylstyrene)-*block*-polyisoprene (PI-*b*-P(PMDSS)-*b*-PI).⁸⁰ The development of such triblock copolymers for the preparation of nanoporous polymers is mainly due to the limits associated with diblock copolymer systems. Indeed, they afford a restricted number of defined morphologies, and in particular the compositional window for the gyroidal phase is very narrow. In contrast, many more morphologies can be encountered when considering triblock copolymers,^{81, 82} as highlighted in **Figure 11**. In this regard, efforts have been put forward to exploit this advantage, notably by fabricating membranes using the polymerization induced phase separation technique.⁸³⁻⁸⁶ This technique is not strictly based on the self-organization of BCPs, it does rely on the chemical dissimilarity between the two constituent blocks of BCPs to template a bicontinuous nanostructure with well-defined pore sizes. Alternatively, another strategy to produce robust membranes from bicontinuous morphologies calls on ABC triblock copolymers. Indeed, such particular macromolecular structures exhibit a higher number of bicontinuous morphologies and larger compositional windows where these morphologies form.⁸⁷⁻⁹⁰ Thus, the addition of a third block (or more) in

BCPs increases the level of self-assembly complexity in bulk. Additionally, it allows for a finer tuning of the morphology. In the case of the ABC triblock copolymers, the number of observable morphologies is greatly increased when compared to AB diblock copolymers, and depends on different parameters, such as the independent volume fractions (f_A , f_B and f_C), the interaction parameters χ_A , χ_B , and χ_C between bound A/B and B/C blocks and unbound A/C segments, respectively. The order of the block in the macromolecular structure (ABC, BAC or ACB) also plays a significant role in the obtained morphology. Bates *et al.* notably summarized some of the obtained morphologies depending on these parameters.⁹

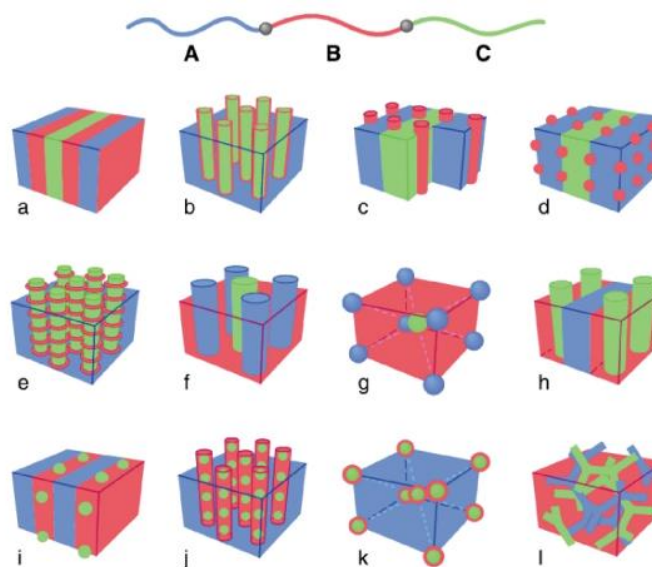


Figure 11. Schematic representation of expected morphologies for linear ABC triblock copolymer. Blocks A, B, and C and their corresponding microdomains from (a) to (l) are represented in blue, red and green, respectively. The combination of block arrangement (ABC, ACB, BAC), composition, and block molar masses play a crucial role in the formation of new morphologies when compared to diblock copolymers. Reprinted from *Polymer*, 44 (22), Park, C.; Yoon, J.; Thomas, E. L., Enabling nanotechnology with self assembled block copolymer patterns, 6725-6760, Copyright 2003, with permission from Elsevier.⁸²

Furthermore, nanoporous structures obtained from diblock copolymers can sometimes suffer from poor mechanical properties. To address this issue consisting in increasing the mechanical robustness of nanostructured polymer thin films to a greater extent, polymer chemists have combined the nature of a block that is rubbery at room temperature, *e.g.* PI, with a block that is glassy at room temperature, *e.g.* PS. Thus, by tailoring the precise composition of these two segments in triblock copolymers, they successfully obtained the desired self-assembled morphology.⁹¹⁻⁹³ This strategy has been notably implemented for PI-*b*-PS-*b*-P4VP,^{91,92} which was considered as a triblock analogue of PS-*b*-P4VP diblock copolymer. Indeed, adding the low glass transition temperature (T_g) PI block⁹⁴ allowed for the preparation of membranes that

were tougher than membranes made from similar diblock templates. The same methodology was implemented by Hillmyer's group to produce nanoporous PS-*b*-PI materials from the corresponding PS-*b*-PI-*b*-PLA triblock copolymer thin films (**Figure 12**).⁹³

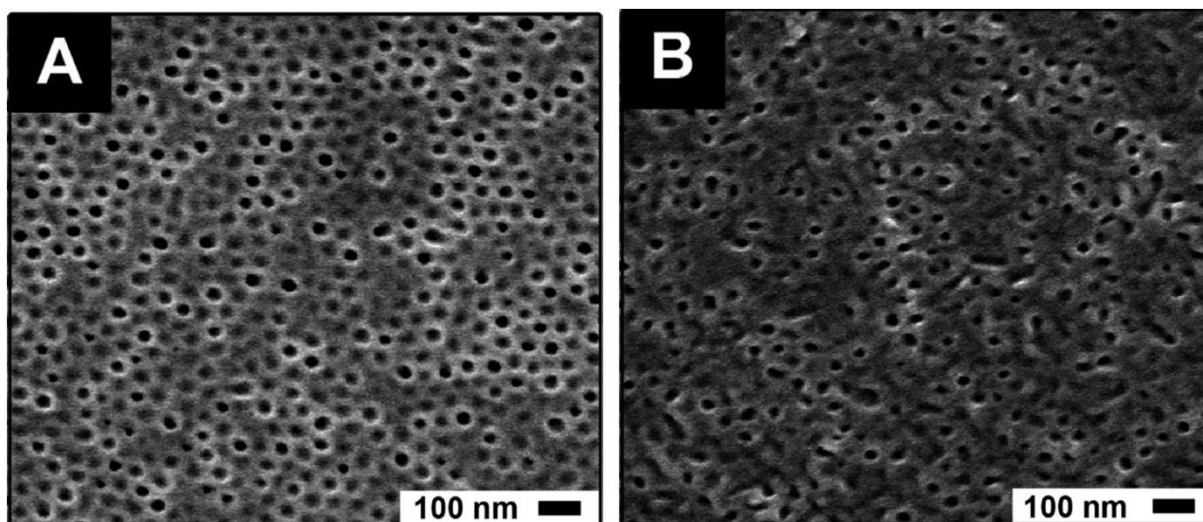


Figure 12. SEM micrographs of the (A) top and (B) bottom of a PS-*b*-PI-*b*-PLA thin film prepared on a NaCl single crystal disk upon PLA hydrolytic degradation. The average pore diameter was determined from SEM as 22 ± 3 nm. Reprinted with permission from ref. ⁹³ Copyright 2013 American Chemical Society.

It is worth mentioning that such a methodology afforded smaller pore sizes when compared to the corresponding diblock counterparts. These examples of triblock polymer design relying on finely tuning the polymer molar mass and constituent blocks in the macromolecular architectures are just two simple handles for polymer scientists to control the nanostructure, as well as the thermal and mechanical properties of the resulting membranes. It is anticipated that even more unique synthetic protocols will allow this arsenal to be expanded greatly in the future. Additionally, Russell and Hawker's research groups jointly highlighted the potential of implementing PS-*b*-PMMA-*b*-PEO triblock copolymers when compared to their diblock counterparts.⁷⁴ Using such triblock polymers indeed permitted to exploit and combine the advantages of both separate diblock systems, *i.e.* the high degree of lateral ordering characteristic of PS-*b*-PEO and the easy degradability of PS-*b*-PMMA diblock copolymer systems, while negating the corresponding drawbacks (*i.e.*, poor degradability of PS-*b*-PEO and no long-range order for PS-*b*-PMMA diblock copolymers).

6.2. Orientation of triblock copolymers

The orientation of triblock copolymers films in bulk is generally achieved through two main processes, either through non-solvent-induced phase separation (NIPS) or self-assembly and non-solvent-induced phase separation (SNIPS). Other methodologies also exist, such as solvent

vapor annealing, but remain limited in the literature.⁹⁵⁻⁹⁷ Experimentally, NIPS consists in casting the polymer solution on a suitable support with a surgical blade in order to get an homogeneous thickness.⁹⁸ This polymer film is then dipped in a coagulation bath that contains the non-solvent. During this step, the solvent will diffuse into the coagulation bath, while the non-solvent diffuses into the film. After some time, the exchange between the non-solvent and the solvent results in a demixing in the solution. Therefore, the resulting membrane is composed of a dense surface layer and a sponge-like sublayer and possesses an appropriate behavior regarding filtration, including high flux, good selectivity, and good mechanical properties. The morphology of the membranes obtained through this methodology depends greatly on the nature of the triblock copolymer, its molar mass, its concentration in solution, the choice of the solvent and of the coagulation bath. Other parameters, such as the temperature of the polymer solution and coagulation bath, evaporation time and relative humidity should also be taken into consideration. SNIPS process is a combination of NIPS and self-assembly. It was pioneered in the 2000's by Abetz and Peinemann for preparing isoporous membranes presenting pores with high-areal density.⁹⁹ The main difference with NIPS relies on an additional evaporation time of the polymer solution casted film before dipping in the non-solvent bath. Such as for NIPS process, the same experimental parameters are still applicable. The success of the SNIPS process, implying the formation of monodispersed pores on the membrane top surface, is generally governed by the state of micellization of block copolymers in solution but also on the morphology of the formed micelles and on their stability. The BCP self-assembly occurs in different steps during this process. First, micelles of the BCP start forming above the critical micelle concentration (CMC) because of unfavorable interactions taking place between the solvent and one of the blocks. Then, this micellization phenomenon continues thanks to the interactions between the BCP blocks and the air-surface interface. Changes in solvent selectivity and solution concentration, due to the variation of the polymer-solvent interactions during the partial solvent evaporation, allow for tuning the initial stage of the emerging structural features and controlling the structure of the micelles. In parallel, the final membrane structure is impacted by the packing of BCP micelles in solution.

Werner and coworkers also proposed the synthesis of PI-*b*-PS-*b*-P4VP terpolymers and their concomitant self-assembly with pentadecylphenol (PDP), giving access to ordered bicontinuous mesoporous morphology upon porogen removal.¹⁰⁰ Indeed, the originality of these investigations lies in the fact that PDP acts simultaneously as an important building block of the assembly but also as a porogenic template.

6.3. Pore chemical functionalization of membranes arising from triblock copolymers

As already demonstrated for nanoporous polymers obtained from diblock copolymers, the chemical nature of the pore surface can also be easily tuned by achieving grafting of (macro)molecules through various chemical strategies upon film casting and microphase separation surface chemistry. Ultra-filtration membrane arising from polystyrene-*b*-poly(methyl methacrylate)-*b*-poly(*tert*-butyl acrylate) (PS-*b*-PMMA-*b*-PtBA) triblock terpolymer have been recently prepared by Park *et al.*⁷⁸ Upon orientation of the terpolymer, cylindrical nanopores were obtained by a simple non-degradative, selective swelling-deswelling process of cylindrical (PMMA-*b*-PtBA) domains, allowing for the pore size to be finely tuned. A subsequent hydrolysis of the PtBA block generated carboxyl functions at the pore surface. The authors notably highlighted the pH-responsive water permeability and their active switching with respect to biomolecules such as Bovine Serum Albumin (BSA). They finally claimed that such membranes could constitute a functional platform to fabricate a stimuli-responsive ultrafiltration membrane using a tunable multiblock copolymer.

Abetz's research group took advantage of the presence of double bonds in PI-*b*-PS-*b*-P4VP to partially graft mercaptoethanol on isoprene units of the triblock terpolymer backbone through photo-triggered radical thiol-ene addition.¹⁰¹ The resulting poly(4-(2-hydroxyethyl-thio)-2-methyl butene-*random*-4-(2-hydroxyethylthio)-3-methyl butene-*random*-isoprene)-*block*-polystyrene-*block*-poly(4-vinylpyridine) (P(HTMB-*r*-I)-*b*-PS-*b*-P4VP) terpolymer possessing miscible end blocks with two different functional groups was then self-assembled. The authors demonstrated that various morphologies could be obtained depending on the experimental conditions implemented to phase-separate the nanodomains of the copolymer. Eventually, they also showed that the hydroxyl and pyridine functions could be modified with 1,3-ethanesultone to produced negatively charged pore surface or pyridine ones with MeI to afford positively charged pore surfaces.

More exotic macromolecular architectures, such as 133 bottlebrush poly(ethylene-*alt*-propylene)-*block*-polystyrene-*block*-poly(ethylene oxide) (PEP-*b*-PS-*b*-PEO) triblock copolymers were produced by Lodge's research group. The synthesis of such macromolecular structures was achieved through sequential ring opening metathesis polymerization (ROMP) of norbornene-appended PEP, PS and PEO macromonomers. By varying the volume fraction of each block, the authors managed to obtained core-shell double gyroid nanostructures. The authors highlighted that their studies brought new synthetic opportunities in the research field associated with applying facile ROMP chemistry to multiblock bottlebrush polymers.¹⁰² The authors demonstrated that as-functionalized nanopores arising from the self-assembled triblock

terpolymer acted as target-specific functional soft nanochannels, due to swelling of the polyelectrolyte blocks in a hydrated state. The functional membranes obtained notably showed unprecedented separation selectivity for small molecules depending on their size and/or charge. The membranes based on these tailor-made triblock terpolymer may represent a potential solution for preparing next generation nanofiltration membranes.

In conclusion, the use of ABC triblock terpolymers possessing a terminal etchable block and a central functionalized one as nanostructured precursors to nanoporous frameworks constitutes an elegant means to tailor pore surface chemistry and morphology. The development of such systems enables to overcome certain issues encountered with diblock systems, such as the difficulty to access to gyroid morphology or the poor mechanical properties of corresponding nanoporous structures sometimes observed with high T_g blocks. It should also be stressed that the nature of the “middle” block has a suitable hydrophilic/hydrophobic character so as not to disturb the nanostructuring of the BCPs during the orientation process.

7. Applications of nanoporous materials derived from di- and tri-block copolymers

During the last decade, different research groups have rapidly expanded the scope of nanoporous polymers arising from block copolymers to design advanced materials for various high added value applications, including supports for heterogeneous catalysis,^{37, 103, 104} responsive (biocatalytic) (ultra)filtration membranes,^{93, 105-108} nanopatterns,^{79, 109, 110} semiconductors¹¹¹ and electrode materials,¹¹² materials for electrical energy storage.¹¹³

7.1. Nanoporous materials as catalytic heterogeneous supports

Two different studies reported on the preparation of nanoporous polymer hollow fibers¹⁰⁴ or thin films³⁷ prepared from block copolymers. In both cases, the authors immobilized gold nanoparticles at the pore surface of these materials, but in different ways. While the first report required the post-etching functionalization of the remaining polystyrene thin film exhibiting aldehyde functions at the pore surface through a reductive amination with tetraethylenepentamine, the second one relied on the coordination of Au^{3+} cations to the nitrogen lone pair of the poly(4-vinylpyridine) (P4VP) block from a PS-*b*-P4VP diblock copolymer. Successive assays on the catalytic activity of such hybrid materials were demonstrated by immersing either thin film or hollow fibers within a solution of *p*-nitrophenol containing a large excess of sodium borohydride. Successful reduction into the corresponding amine derivative was observed. Poupart *et al.*³⁷ also smartly showed that a cascade catalytic reaction, consisting of a boronic acid C–C homocoupling followed by nitroarene reduction from a *m*-nitrophenylboronic acid, could be successfully achieved with these hybrid nanoreactors.

7.2. Nanoporous materials as responsive filtration membranes

Weidman *et al.*³² reported on the implementation of PI-*b*-PS-*b*-PDMA nanoporous thin film suitably functionalized with glutathione or cysteamine for the capture of heavy metal cations among which pollutant ones, such as lead and cadmium (**Figure 13**). Removal rates of ions in excess of 95% and even higher were observed when flow-through configuration was envisioned. After such capture experiments, the materials were repeatedly regenerated quickly and no loss in capacity was found out by the authors. The authors claimed that these membranes provide a sustainable platform for the efficient purification of lead- and cadmium-contaminated water sources to safe levels.

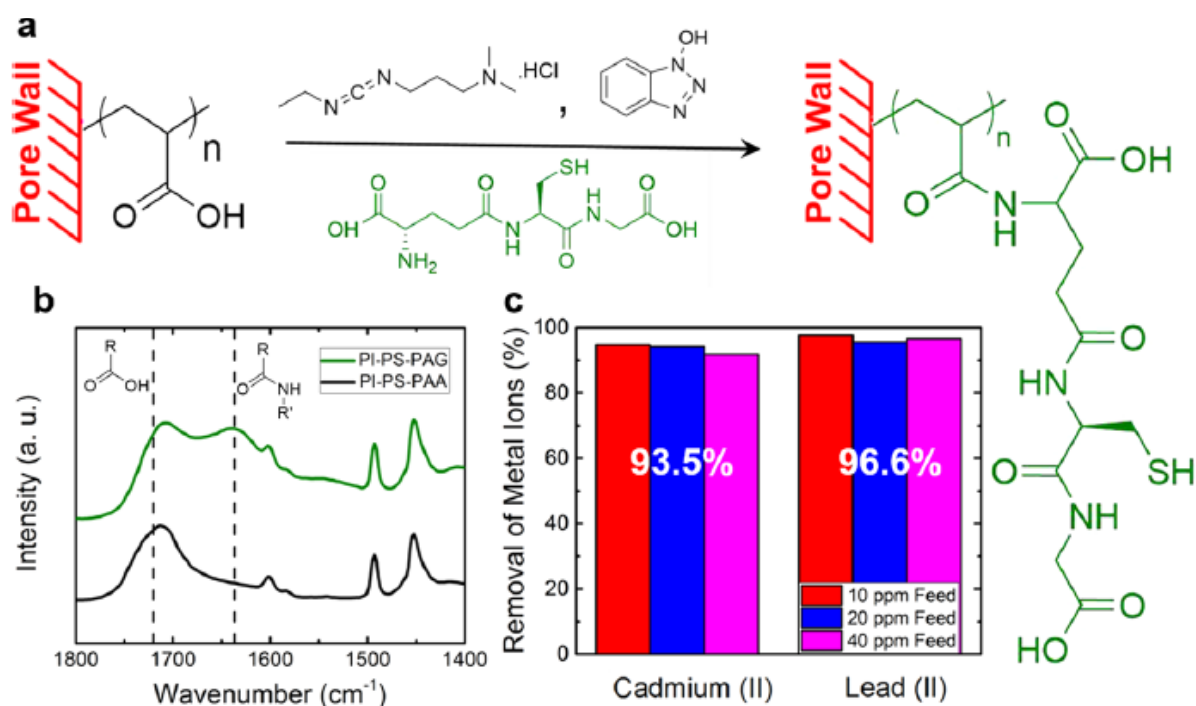


Figure 13. (a) Schematic synthetic pathway for the functionalization of acrylic acid lining pore walls of the thin polymer film with glutathione. (b) FTIR spectra of the as-functionalized membranes before (black) and after (green) coupling with glutathione. The peak at 1640 cm⁻¹, corresponding to ν_{C=O} amide highlights the successful coupling of the peptide. (c) Graphic representing the removal of Cd²⁺ or Pb²⁺ ions from aqueous solutions containing 10 (red bar), 20 (blue bar), and 40 ppm (pink bar) charge of these ions. The average Cd²⁺ and Pb²⁺ removal was found to be 93.5 and 96.6%, respectively, as determined by ICP analysis. Reprinted with permission from ref. ³² Copyright 2017 American Chemical Society.

Peinemann's research group developed original integral asymmetric membranes in a fast and one-step process by combining the self-assembly of an amphiphilic PS-*b*-P4VP diblock copolymer with nonsolvent-induced phase separation.¹⁰⁸ The authors notably found out a structure composed of a thin layer of densely packed highly ordered cylindrical channels with uniform pore sizes perpendicular to the surface on top of a nonordered spongelike layer. Such as-prepared membrane displayed a water flux of more than 3200 L.m⁻².h⁻¹.bar⁻¹, value at least

an order of magnitude higher than the water fluxes of commercially available membranes having comparable pore sizes. This makes such membrane particularly appropriate to size-selective and charge-based separation of biomolecules. The authors assessed the performance of these membranes by conducting diffusion experiments at pH 7.4 (physiological pH) using bovine serum albumin (BSA) and globulin- γ , two proteins with different diameters but too close in size (2-fold difference in molecular mass). The latter were efficiently separated via conventional dialysis membrane processes. The ratio of the diffusion rate of each protein was found to be equal to 87, the highest value reported to date. charge-based diffusive transport and separation of two proteins of similar molecular weight, namely BSA and bovine hemoglobin (BHb), through the membranes was also analyzed as a function of the external pH. The membranes achieved a selectivity of about 10 at pH 4.7, i.e. the isoelectric point (pI) of BSA. With a modified membrane preliminarily positively charged, BSA was completely blocked when the pH was 7.0, i.e. the pI of BHb, while BHb was completely blocked at pH 4.7. The authors thus highlighted the potential of these asymmetric membranes to efficiently separate large biomolecules/pharmaceuticals in bioscience, biotechnology, and biomedicine applications.

7.3. Nanoporous materials for nanolithography

Block copolymer assisted nanopatterning have been widely developed for the preparation of inorganic nanomaterials. Hardy *et al.* elegantly demonstrated that highly ordered iron oxide nanoparticles (α -Fe₂O₃) can be produced through a synthetic path involving the preparation of thin films from well-defined ferrocene-containing triblock copolymers synthesized by atom transfer radical polymerization.¹⁰⁹ Upon self-assembly into highly ordered hexagonal arrays of cylinders via solvent annealing, those thin films were further used as a template. Successive UV/ozonolysis and thermal pyrolysis treatments allowed for the obtention of the inorganic nanomaterials.

Another smart strategy was developed by Hadjichristidis' research group for the preparation of 19 nm high silica rings.¹¹⁰ In this study, a pattern transfer from a self-assembled PB-*b*-PS-*b*-PMMA triblock terpolymer thin film was investigated. Polymers of different total molecular weight were designed so as to get morphologies consisting of PMMA-core/PS-shell cylinders in a PB matrix. Thus, thin films with vertically oriented cylinders were formed by tuning the solvent-annealing conditions and the film thickness. Using selective etching conditions allowed the PMMA cylinder cores and the PB matrix to be successfully removed, thus leaving an array of PS rings. A final reactive ion etching step allowed the transfer of ring pattern into a silica

film, allowing for the formation of silica rings. Both These studies illustrate the design and use of block copolymers for self-assembled lithography.

7.4. Nanoporous materials for energy storage applications

Wiesner's research group has nicely expanded the scope of triblock copolymers towards the preparation of smart electrical energy storage systems. This application required to produce co-continuous and interpenetrating solid-state nano-3-D Li-ion/sulfur hybrid systems stemming from PI-*b*-PS-*b*-PEO, as depicted in **Figure 14**.¹¹³ Those advanced systems demonstrated battery-like characteristics with stable open circuit voltage, reversible discharge voltage and capacity, and orders of magnitude decreases in footprint area over two-dimensional thin layer designs.

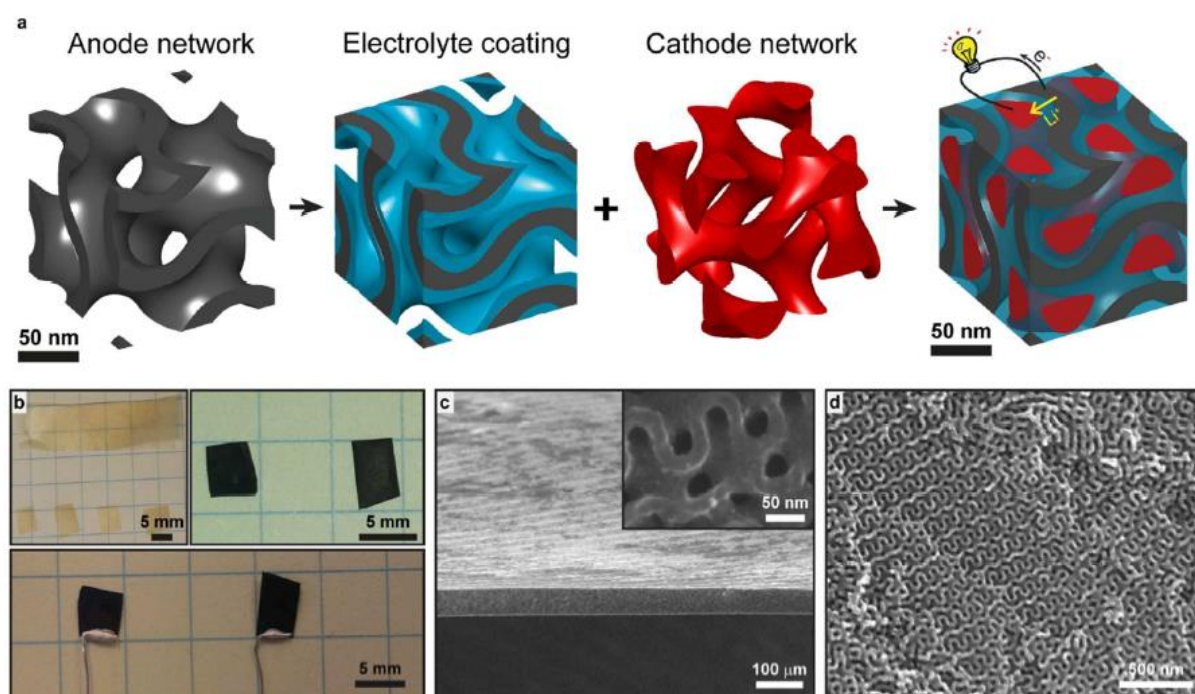


Figure 14. (a) Schematic cartoon of the principle of synthetic pathway adopted for the assembly of a penta-continuous interpenetrating and nanostructured hybrid from double gyroidal mesoporous carbon monoliths: A redox-active and conductive carbon anode with gyroidal 3-D structure and finite wall thickness (black) is conformally coated with nanoscaled poly(phenylene oxide) polymer electrolyte (blue), the two remaining interpenetrating mesoporous network channels were back-filled with a redox-active and conductive cathode (red) consisting in a composite of sulfur and poly(3,4-ethylenedioxythiophene). (b) Photographs of as-made BCP-organic hybrids (top left), double gyroidal mesoporous carbon monoliths after carbonization (top right), and double gyroidal mesoporous carbon monoliths electrically contacted in edge-on geometry (bottom). (c), (d) SEM micrographs of a uniform thin film obtained from a double gyroidal mesoporous carbon monolith (c), open and accessible gyroidal mesoporosity can be observed from the surface of these thin film (c, inset) but also from the cross-section (d). Reprinted with permission from ref. ¹¹³ Copyright 2018 Royal Society of Chemistry.

Very recently, Ito *et al.*¹¹⁴ implemented a synthetic strategy based on ONB junction for preparing PS-*b*-PEO diblock copolymers. The authors used such copolymers to prepare thin films on gold substrate. Upon PEO sacrificial block removal, the resulting nanoporous polymers could be eventually further modified with thiolate self-assembled monolayers (SAMs) and thus could be developed as electrode materials.

8. Conclusion

The preparation of functional ordered nanoporous frameworks from semi-degradable diblock or triblock copolymers necessitates to tailor the molecular characteristics of the architectures, which is now easily accessible through the development of controlled radical polymerization techniques. While harsh experimental conditions have firstly been necessary to etch the sacrificial block from microphase-separated diblock copolymers, an alternative and somehow smarter strategy, deeply investigated in the last years, relies on the selective cleavage of the chemical junction present between both blocks. It allows for mild etching conditions to be implemented, while giving the opportunity to further functionalize the available chemical functions present at the pore surface with (macro)molecules of interest, depending on the targeted application. The implementation of triblock rather than diblock copolymers presents some interesting advantages. It enables an easier access to some morphologies that are impossible to access with diblock analogues. Additionally, the third block also offers the possibility to tune the thermal and mechanical properties of the resulting nanoporous materials. In the case of triblock copolymers, the strategy to align the microphase separated domains of the macromolecules mainly relies on non-solvent-induced phase separation or concomitant self-assembly and non-solvent-induced phase separation. This allows to produce a plethora of membrane systems for (ultra)filtration, but also to nanomaterials that have been shown to be present some interesting features in diverse high added value research areas, including batteries, semiconductors, templates for nanolithography, synthesis of electrodes, etc.

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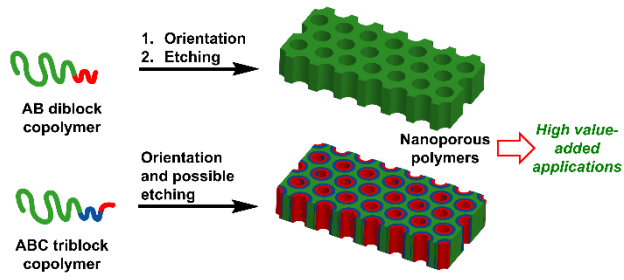
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