Molecular engineering of the block copolymer junction to control chemistry of the pore in nanoporous thin films

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Molecular Engineering of the Block Copolymer Junction to Control Chemistry of the Pore in Nanoporous Thin Films

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Doctor of Sciences

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# Contents

Summary .................................................................................................................. I
Zusammenfassung ..................................................................................................... II

Chapter 1: Introduction ......................................................................................... 1
Aim and Organization of this Thesis ................................................................. 8
References ........................................................................................................... 9

Chapter 2: Supramolecular Mimics of Phase Separating Covalent Diblock Copolymers
2.1 Introduction .................................................................................................... 13
2.2 Results and Discussion ................................................................................ 16
2.3 Conclusions .................................................................................................. 22
2.4 Experimental Details .................................................................................... 23
2.5 References ..................................................................................................... 27

Chapter 3: Synthesis and Thin Film Assembly of Dynamic Covalent Diblock Copolymers
3.1 Introduction .................................................................................................... 31
3.2 Results and Discussion ................................................................................ 33
3.3 Conclusions .................................................................................................. 41
3.4 Experimental Details .................................................................................... 41
3.5 References ..................................................................................................... 47

4.1 Introduction .................................................................................................... 49
4.2 Results and Discussion ................................................................................ 51
4.3 Conclusions .................................................................................................. 59
4.4 Experimental Details .................................................................................... 60
4.5 References ..................................................................................................... 64

Chapter 5: Assembly of Interacting Binary Blends of Diblock Copolymers in Thin Films
5.1 Introduction .................................................................................................... 67
5.2 Results and Discussion ................................................................................ 69
5.3 Conclusions .................................................................................................. 78
5.4 Experimental Details .................................................................................... 79
5.5 References ..................................................................................................... 82

General Conclusions .......................................................................................... 87
Appendix ............................................................................................................... 89
Curriculum Vitae .................................................................................................. 91
A nanoporous membrane contains enclosed channels spanning the thickness of the membrane material. The diameter of these channels can vary from several to a few hundred nanometers. Due to these pores, a nanoporous thin film can be used as a size-selective filter as molecules/objects with lower dimensions than the pore diameter can pass through them whereas the larger ones cannot. An interesting possibility occurs when the surface chemistry of a nanopore is modified. This allows for additional parameters, such as charge and hydrophobicity, to come into play in deciding the efficacy of a membrane. If the surface chemistry of the pore-wall could indeed be controlled, then many other interesting avenues come to the fore. For instance, a catalyst, such as an enzyme, can be immobilized onto the pore wall. In this manner, molecular discrimination by the pores, based upon size, charge, and hydrophobicity, can be combined with catalytic activity of the enzymes. It is for these reasons that development of methods by which the surface chemistry of a nanopore can be tailored are of considerable significance. Towards this end, the present thesis explores control strategies over surface chemistry of the pores in nanoporous thin films derived from self-assembling block copolymer precursors. In general, the block copolymer building blocks are carefully designed to have incompatible blocks, asymmetric block lengths, and a reversible copolymer junction. Self-assembly of such copolymers results in nanostructured thin films exhibiting highly ordered cylindrical morphology. Removal of the nanosized cylinders by reversing the reversible copolymer linkage then affords ordered nanoporous membranes that contain chemically reactive functionalities within the nanopores. These functional groups can be subjected to chemical manipulation (such as change in chemical charge), covalent functionalization through reforming the reversible linkage, or non-covalent functionalization through establishing supramolecular contacts.
Chapter 1: Introduction

Self-assembly of block copolymers is a promising route to creating nanoporous materials of controlled pore dimensions. This chapter briefly describes the two major pathways adopted for transforming a self-assembled diblock copolymer thin film into a nanoporous membrane and relates these studies to the working hypothesis and ideological evolution of the present thesis.

Block copolymers are composed of two or more chemically different polymer chains, which are covalently bound together. In the case of block copolymers featuring two immiscible blocks, phase separation of the two segments on the macro scale is not possible as both blocks cannot detach from one another and hence microphase separation into ordered microstructures with length scales of the order of ten to a hundred nanometer occurs.\(^1\)\(^2\) Depending on the Flory-Huggins interaction parameter between the monomer units, the length of the block copolymers and the composition, different structures are formed due to the balancing act of the enthalpic interfacial energy between the blocks and the entropic chain stretching energy of the individual blocks. Body centered cubic packed spheres, hexagonally packed cylinders, and alternating lamellae are the most common microstructures found for conformationally symmetric diblock copolymers. These nanostructured thin films can be transformed into nanoporous materials upon selective removal of the minor polymer domains (Figure 1.1).\(^2\)\(^3\) In this way, highly ordered nanoporous thin films of
defined pore sizes and narrow pore size distribution can be obtained. Initially, removal of the minor domain was achieved by degradation of the polymer backbone. For instance, poly(methyl methacrylate) (PMMA) domains were removed via UV degradation.\textsuperscript{4} Ozonolysis was the method of choice to degrade poly(isoprene) (PI) and poly(butadiene) (PBD) segments.\textsuperscript{5} Poly(lactide) (PLA) blocks were removed by chemical etching methods.\textsuperscript{6} Finally, strong acidic conditions could be employed for the removal of poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) polymers.\textsuperscript{7} These processes are sufficient for converting the polymer thin film into a nanoporous structure. However, there are issues associated with these systems. For example, harsh etching conditions may broaden the pore size distribution. More importantly, the nature of the functional group at the end of an etching process remains ill-defined and cannot be selected and controlled precisely. For example, in the widely utilized case of PMMA, UV degradation can lead to the formation of, among others, terminal epoxide, internal epoxide, \textsuperscript{1,2,3}trisubstituted and \textsuperscript{1,2}disubstituted internal olefin, \textsuperscript{1,2}disubstituted terminal olefin, aldehyde, and geminal-dimethylester chain-end functionalities.\textsuperscript{8}

![Diagram of diblock copolymer assembly and removal of the minor polymer block](image)

**Figure 1.1.** Assembly of a diblock copolymer into cylindrical morphology and removal of the cylindrical domains to yield a nanoporous thin film.

In an alternative approach, cleavage of the copolymer junction – rather than polymer backbone – is shown to efficiently generate nanoporous materials from the self-assembled block copolymer thin film. In this approach, only one reaction – breakage of the copolymer junction – is required for selective removal of the minor
polymer block. Penelle and coworkers first demonstrated this strategy by employing a poly(styrene)-block-poly(methyl methacrylate) copolymer connected through an anthracene dimer (Scheme 1.1). The synthesis of this dimer required 150 hours of photoirradiation conditions. Clearly, PS and PMMA homodimers were also produced during the course of the reaction. Nonetheless, films were prepared and annealed at 170 °C. At this temperature, however, the anthracene photodimer thermally reverted back to the homopolymers. Hence, the temperature was decreased to 135 °C. This lowering of annealing temperature limited the extent of homopolymer formation (to about 30%) and allowed for polymer self-assembly into a cylindrical morphology. The minor domains were then removed under thermal conditions. However, no chemistry was performed within the pores.

![Scheme 1.1](image)

**Scheme 1.1.** Scission of PS-PMMA diblock copolymer connected through an anthracene dimer into constituent homopolymers.

To improve upon this concept, Venkataraman and coworkers devised an elegant strategy. In this strategy, a triphenylmethyl ether bond was established as a copolymer junction connecting the PS and PEG homopolymers (Scheme 1.2). Once the diblock copolymer assembled into a nanostructured morphology in thin films, the trityl ether linkage could be broken by exposure to the vapors of trifluoroacetic acid (TFA). In this way, a highly ordered nanoporous thin film could be obtained. The trityl alcohol groups, however, are known to be the least reactive among the alcohol functionalities. Therefore, the pore-functionalization concept is impractical for this system.
Scheme 1.2. Cleavage of a trityl-ether linked diblock copolymer into PEG and PS homopolymers.

To circumvent this reactivity limitation, Hawker and coworkers established synthesis and self-assembly of PEG-b-PS copolymers connected through an acetal linkage (Scheme 1.3). This pathway led to the formation of cylindrically ordered nanoporous thin films containing a primary hydroxyl group within the nanopore. However, pore-wall modifications were not studied.

Scheme 1.3. Use of an acetal linkage to connect phase separating PEG and PS polymers and their breakage under acidic conditions.

In a different approach, Russell and Thayumanavan used disulphide bond formation to prepare highly ordered nanostructured templates for composite materials synthesis. To achieve this, dithiol-linked PS-b-PEG copolymer was synthesized and allowed to assemble in thin films (Scheme 1.4). The PEG block was then removed under reductive conditions and the thiol ligands were used to coat the pore surface with metallic gold. Covalent chemical modifications of the thiol groups were, however, not pursued.

Scheme 1.4. Disulfide-linked PEG-PS diblock copolymer and their cleavage under reductive conditions.
In a considerable deviation from the aforementioned pore generation strategies, Moon and coworkers showed that use of an ortho-nitro benzyl alcohol-linked (Scheme 1.5) phase separating diblock copolymer allowed for copolymer linkage to be cleaved under photolytic conditions in a thin film. Gohy and coworkers have adopted this strategy in the preparation of a variety of reactive membranes.

Scheme 1.5. Utilizing light as an external stimulus to cleave a diblock copolymer into its homopolymer constituents.

At the beginning of this thesis work, we envisaged that phase separating homopolymers connected via a supramolecular reversible linkage – rather than the classic covalent bond – would serve as superior building blocks for nanoporous thin film preparation. We hypothesized that supramolecular linkages, such as those based upon hydrogen bonding interactions, would have significant advantages over use of (traditional) diblock copolymers in the present context. For example, we anticipated that the proposed strategy would allow for complete and total removal of the minor polymer domain under non-invasive and mild conditions from the organized nanostructured thin film. This expectation originated from the knowledge that hydrogen-bonding interactions can be broken in the presence of a hydrogen-bonding-competing solvent such as water. Therefore, the films could be made porous in water and under neutral conditions. Due to the mild nature of such a cleavage reaction, we also expected that the porosity generation process could be performed at room temperature. It should be noted that a complete removal of the minor polymer domain is critical to the structural integrity of the pores. Furthermore, a mild and aqueous procedure that can be carried out under ambient conditions (without
requiring heat energy) addresses the timely need of establishing environmentally friendly and sustainable technological processes. Another advantage of the proposed system would be that the pore-wall could be decorated with a known and well-defined functionality (hydrogen bond donor/acceptor) that can be predetermined as per the requirement. This aspect relates to the question of imprinting the pore-wall with a chemically well defined, predetermined, and tunable functional group. Finally, the modular nature of the supramolecular diblocks was expected to allow the use of end-functional homopolymers that can be synthesized with greater structural perfection and purity over synthesis of covalent diblock copolymers. This final aspect relates to the modularity of the system in which various homopolymer building blocks with a known end-group can be synthesized separately and combined in different ways (a Lego approach) to access membranes having different functionalities in the nanopores. It, however, became clear that supramolecular diblock copolymers connected through a hetero-complementary quadruple hydrogen bonding motif yielded films with low lateral order and broad polydispersity of the cylindrical domains (Chapter 2). Although these results were remarkable as they demonstrated that supramolecular analogues of classic covalent diblock copolymers retained their ability to microphase separate in thin film with comparable feature sizes. The high polydispersity of the nanostructures did not encourage us to use these templates for the preparation of nanoporous materials. Therefore, we moved on to the idea of using a dynamic-covalent linkage at the block copolymer junction. Like supramolecular interactions, dynamic covalent bonds can be formed and broken under mild conditions, however they have significantly increased stability. For example, an oxy-imine derivative – the product of a reaction between oxy-amine and aldehyde functional groups – is stable to a variety of chemical manipulations and chromatographic purifications, yet the imine linkage in such compounds can be reversed quantitatively under certain experimental conditions (pH, temperature, solvent). We hypothesized that in the present context, the stability of the dynamic covalent bond would allow for the following effects that were unattainable in the aforementioned supramolecular system: a) synthesis and purification of block
copolymers linked \textit{via} a reversible linkage, b) thin film annealing under thermal and/or high humidity conditions, and c) attaining nanostructured morphology with long-range lateral order. The power of using dynamic covalent bonds could then be realized by reversal of the dynamic imine bond which leads not only to removal of one of the blocks but also leaves behind a well-defined functional groups – either oxy-amine or aldehyde – at the pore surface which is then available for further chemical transformations. This strategy was demonstrated to be a useful tool in the preparation of reactive nanoporous thin films (\textbf{Chapter 3}).\textsuperscript{19} However, use of TFA was deemed necessary to achieve high porosity conditions. Therefore, an improvement of this system was achieved by replacing the oxy-imine linkage with the more sensitive hydrazone-based dynamic covalent bond. This strategy indeed led to a system in which the porosity could be generated in water and at room temperature, and the film could be functionalized in the gas phase, without necessitating a solvent, a coupling reagent, or heating (\textbf{Chapter 4}).\textsuperscript{20} However, it was recognized that all of these systems suffered from the low availability and low number of reactive sites per unit area.\textsuperscript{21} This is due to the fact that only one reactive site is generated upon cleavage of a copolymer precursor. Moreover, although these functionalities must be at the interface, some of them are likely to be buried within the polymer matrix. Thus, in order to increase the number of reactive group per unit area and their availability for further chemical modifications, the lessons learned through the activities of \textbf{Chapters 2-4} of this thesis were combined to establish a system in which multiple (~15) supramolecular interactions were used to constitute a phase separating copolymer “linkage” (\textbf{Chapter 5}). This system was found to be an optimum system that offered good order of the nanostructured morphology, porosity generation at room temperature and in aqueous conditions, and a high number of reactive and available sites within the nanopores.\textsuperscript{22}
Aim and Organization of this Thesis

If surface chemistry of a nanopore can be controlled and modified, enhanced separations based on molecular properties such as charge and hydrophobicity – in addition to size – can, in principle, be achieved. Such advanced porous materials with tailored pore-surface chemistry will therefore allow for more selective and effective separation/filtration/reaction principles to be studied. This will broaden our knowledge as well as the scope of applications in which these nanoporous materials will be useful. This thesis, therefore, strives at developing strategies that can allow for total control over surface chemistry of a nanopore in porous thin films prepared from the (known) assembling properties of phase-separating block copolymers.

Chapter 2
This chapter examines the possibility of replacing the carbon-carbon (C-C) covalent bond-based copolymer junction with a hydrogen bonding motif in the molecular design of phase-separating diblock copolymer.

Chapter 3
This chapter describes application of the concepts of dynamic covalent chemistry towards preparation of reactive nanoporous thin films.

Chapter 4
This chapter elaborates upon an improved molecular design of the materials presented in the third chapter.

Chapter 5
In this chapter, binary blends of interacting block copolymers are recognized as highly promising building blocks for the preparation of the nanoporous materials carrying a large number of available reactive sites within the nanopore.
References


21. Hillmyer and coworkers determined the areal density of functional groups on the pore wall to be 0.25/nm$^2$ by using Brunauer-Emmett-Teller (BET) surface area measurement method. In this case, the polymer molecular weight was 37 kDa. Nonetheless, by conducting water uptake experiments it was concluded that the functional group density at the pore wall was insufficient to change the surface properties of the nanopore: A. S. Zalusky, R. Olayo-Valles, J. H. Wolf and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2002, 124, 12761.

In this chapter, we explore the supramolecular association and phase separation properties of non-covalent analogues of polystyrene-\textit{b}-polyethylene glycol (PS-\textit{b}-PEG) and polystyrene-\textit{b}-polyisoprene (PS-\textit{b}-PI) diblock copolymers. For this purpose, PS homopolymer is end-functionalized with a quadruple hydrogen bonding unit and PEG and PI homopolymers are end-functionalized with a hetero-complementary hydrogen bonding group. Hetero-dimerization between the complementary chain ends of the respective homopolymers furnishes supramolecular (s) PS-\textit{s}-PEG and PS-\textit{s}-PI diblock copolymers, with phase-separation studies in thin films and bulk demonstrating that the non-covalent block copolymers are capable of self-organizing into nanostructured morphologies reminiscent of their covalent analogues.

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2.1 Introduction

The ability of block copolymers to self-assemble and generate a variety of nanostructured morphologies in thin films is a fascinating area of research with academic and industrial significance.\textsuperscript{1,2} Typically, two chemically dissimilar monomer sequences are connected through a covalent bond and, depending upon the
ratio of the volumes and $\chi N$ (where $N$ is the degree of polymerization and $\chi$ is the normalized segment-segment repulsion), different nanostructures are formed. Body centered cubic packed spheres, alternating lamellae, and hexagonally packed cylinders are commonly observed in the case of random-coil, linear diblock copolymers. To overcome the limitations of covalent block copolymers, it is envisaged that block copolymers based on side-chain or backbone non-covalent interactions$^{3-4}$ may lead to attractive new properties due to the tunable interplay between association/dissociation of the supramolecular recognition units and the accompanying micro/macro phase separation of the polymer domains. Since supramolecular interactions can be formed and broken reversibly under a variety of external conditions such as temperature, the polymer thin films may exhibit stimuli responsiveness.$^{5-7}$ Additionally, due to reversibility and exchange dynamics of the non-covalent interactions, supramolecular copolymer thin films with cylindrical morphology can potentially give rise to nanoporous membranes featuring recognition sites arrayed within the nanopores.$^8$

Various research groups have combined non-covalent interactions (hydrogen bonding, ionic interactions, and metal coordination)$^9-21$ with microphase separation properties of block copolymers. For example, blending of AB/C, AB/CD, ABA/CD, ABA/CDC, or ABC/AD types of block copolymers in which two blocks carry complementary supramolecular interacting sites either as homopolymers or copolymer sequences are demonstrated to produce a wide range of nanostructured morphologies.$^{11-15}$ Mixing of small molecules capable of forming non-covalent bonds to one of the polymer blocks is another powerful tool to produce thin films with structural hierarchy.$^9b,9d,16$ With polymers bearing a hydrogen bonding group at either one or both chain ends being used.$^6,17-19$ While considering the AB type of supramolecular diblock copolymers, in some of the known examples,$^{17,21}$ molecular recognition units constitute a significant fraction of the polymer chain and it is known that crystallization and/or phase separation of the end groups can influence the bulk properties.$^{22}$ In another example, unwanted homodimerization of one of the recognition sites can lead to a mixture of AA and AB types of copolymers to be
formed in bulk state. Furthermore, in some cases, polymers with low $\chi$ parameter are combined, while those utilizing strongly phase separating polymers employ supramolecular interactions of limited reversibility. Therefore, properties of strict non-covalent mimics of a strongly phase separating AB type of covalent diblock copolymer remain unexplored. Towards this end, in this chapter, we describe the synthesis and self-assembling properties of supramolecular diblock copolymers in which: a) the polymer chains, polystyrene (PS) and polyethylene glycol (PEG)/polyisoprene (PI), have a strong tendency to phase separate, b) the recognition groups are placed at one chain end and contain the necessary information to form a heterodimer exclusively via high strength yet completely reversible quadruple hydrogen bonding interactions, and c) the recognition groups do not contribute appreciably in terms of mass and volume to the final diblock copolymer composition but do have significantly different polarities. In addressing all of these features, a major advance in the understanding of supramolecular diblock copolymers is expected with the target systems being supramolecular mimics of the classic covalent PEG-$b$-PS and PI-$b$-PS diblock copolymers that have received widespread attention in the literature.
2.2 Results and Discussion

2.2.1 Molecular Design and Synthesis

In order to examine strongly phase separating materials, PS (~13 kDa) was selected as one component and either PEG or PI (~5-6 kDa) as the second block of the supramolecular system. The first challenge of overcoming the strong tendency for macrophase separation necessitated that the association strength of the supramolecular junction should be high. A high association constant will also be critical for polar systems such as PEG in which both the heteroatoms along the main chain and residual/adsorbed water can disrupt H-bonding. For this reason, Zimmerman’s naphthyridine-guanosine heterodimer was chosen as the supramolecular pair which acts as the junction point between the separate homopolymer blocks.\(^{25-26}\) Weck and coworkers have established the utility of this dimer towards preparation of non-covalent block copolymers based on ring opening metathesis polymerization (\(K_a \approx 2 \times\)
$10^4$ M$^{-1}$. PS, 1 ($M_n = 13100$ g.mol$^{-1}$, $M_w = 14600$ g.mol$^{-1}$, $M_w/M_n = 1.11$) was prepared by atom transfer radical polymerization using a 2,7-diamido-1,8-naphthyridine based polymerization initiator (Scheme 2.1). Synthesis of the complementary PEG, 2 ($M_n = 4200$ g.mol$^{-1}$, $M_w = 5000$ g.mol$^{-1}$, $M_w/M_n = 1.19$), and PI, 3 ($M_n = 5500$ g.mol$^{-1}$, $M_w = 6600$ g.mol$^{-1}$, $M_w/M_n = 1.2$), was accomplished via an esterification reaction between commercially available hydroxyl end-functional polymers and the carboxy-functionalized guanosine-urea derivative (Scheme 2.1). The target molar masses and volume ratios of the polymer blocks were designed to yield a cylindrical morphology within a PS matrix after the self-assembly of the supramolecular diblock copolymer in both thin film and bulk states.

Figure 2.1. $^1$H-NMR spectra of the building blocks 1 (A), 2 (B), and 3 (C), and supramolecular diblock copolymers 4 (D) and 5 (E) in CDCl$_3$ at room temperature. The solvent signals are marked with an
Chapter 2

2.2.2 Molecular Recognition in Solution

Initially, molecular recognition events between 1 and 2, and 1 and 3 (Scheme 2.2) were studied in solution with the aid of $^1$H-NMR spectroscopy. The amide proton signals for the building blocks 2 and 3 appeared around 7, 9, and 12 ppm (Figure 2.1) and upon complexation with the PS derivative, 1, in a 1:1 molar ratio, downfield shifts for the amide proton resonances to 9.3 (H$a$), 11.5 (H$b$), 11.9 (H$c$), 12 (H$d$), and 13.65 (H$e$) ppm were observed (Figure 2.1). The shifts and signal positions were in agreement with the literature report$^{27}$ and indicated that the hydrogen bond DAAD (D = donor, A = acceptor) array of 1 recognizes the complementary ADDA array of the building blocks 2 and 3 via quadruple hydrogen bonding interactions to give supramolecular diblock copolymers 4 and 5 in solution.$^{29}$

![UV-Vis spectra of the building blocks 1, 2, 3, and the supramolecular diblock copolymers 4 and 5.](image)

**Figure 2.2.** UV-Vis spectra of the building blocks 1, 2, 3, and the supramolecular diblock copolymers 4 and 5.

To confirm the complexation between the complementary building blocks in
solution, UV-Vis spectroscopy in toluene was also employed. PS 1 exhibited multiple absorption peaks ranging from 310-350 nm while polymers 2 and 3 showed no absorption above 310 nm (Figure 2.2). Mixing polymers 1 and 2, and 1 and 3 in 1:1 molar ratio resulted in the appearance of a new absorption peak at 350 nm. This, as demonstrated by Zimmerman and coworkers,\textsuperscript{26} suggested formation of the supramolecular diblock copolymers 4 and 5 via heterodimerization of the recognition units and corroborated the above $^1$H-NMR studies.

**2.2.3 Self-Assembly in Thin Films**

Having demonstrated supramolecular assembly in solution, thin films (~100 nm) of 4 and 5 were then cast on silicon substrates from a toluene solution and the surface morphology was studied by AFM in order to understand bulk versus solution assembly. For the thin films of 4, AFM revealed microphase separated domains of PEG-guanosine (~20-25 nm) dispersed in a matrix of PS-naphthyridine in an apparent cylindrical morphology (Figure 2.3). In order to confirm that the microphase separation was due to the hydrogen bonding interaction between the chain ends, thin films cast from a blend of unfuncionalized PEG and PS of similar molecular weights were studied. As seen in Figure 2.3, these films showed gross macrophase separated morphology. Significantly, comparison with the corresponding covalent PS-\textit{b}-PEG block copolymer of similar molecular weight shows microphase separation with feature sizes similar to that for the supramolecular system. The primary difference between the covalent and non-covalent block copolymers is the regularity with the annealed, covalent system showing enhanced long-range order.\textsuperscript{30} Thin films of 5 showed featureless and homogenous film morphology after spin casting process (Figure 2.4). Since the surface energy of PI is significantly lower than PS, it is likely that the surface is completely covered by PI.
Figure 2.3. AFM height (left) and phase (right) images of supramolecular diblock copolymer 4 (top), a blend of un-functionalized PEG$_{5kDa}$ and PS$_{13kDa}$ (middle), and a covalent diblock copolymer (PEG$_{6kDa}$-b-PS$_{13kDa}$) (bottom).
2.2.4 Self-Assembly in Bulk

Bulk samples were then prepared by slow evaporation of a 1.5wt% toluene solution of 4 or 5. These samples were then sectioned into thin slices (~50 nm) and stained with RuO$_4$ (for 4) or OsO$_4$ (for 5). Multiple thin slices from the same bulk sample were then imaged using TEM. Images from 4 showed a microphase separated...
structure (Figure 2.5) and since RuO$_4$ is more selective for PEG than PS,$^{24a}$ the hydrophilic PEG domains appear as dark spots. Samples from 5 showed similar results with PI being the minor phase and appearing dark due to the staining while PS is the major phase and forms a lighter colored matrix (Figure 2.6).

![Figure 2.6. TEM image obtained via cryo-microtoming of a bulk sample of PS-$s$-PI diblock copolymer 5.](image)

### 2.3 Conclusions

By tuning the strength of a single supramolecular association at the junction point between chain end functionalized homopolymers of strongly phase separating PS/PEG and PS/PI pairs, mimics of the covalent diblock copolymers have been prepared. Exploiting a strong and hetero-complementary molecular recognition pair allows self-organization of these polymers resulting in nanostructured materials. This demonstrates that supramolecular analogues of PS-$b$-PEG and PS-$b$-PI block copolymers can retain their ability to microphase separate in both thin film and bulk materials with comparable feature sizes.

These films, however, were not used as templates for the preparation of nanoporous materials due to high polydispersity of the nanostructures. The next chapters present systems that do not suffer from this issue.
Chapter 2

2.4 Experimental Details

2.4.1 General Methods and Materials

Polyethylene glycol monomethyl ether \((M_n = 5000 \ \text{g.mol}^{-1})\), hydroxyl terminated 1,4-rich polyisoprene, \((M_n = 6500 \ \text{g.mol}^{-1})\), 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide hydrochloride (EDCI.HCl), 1-ethyl-1-hydroxybenzotriazole (HOBt), 4-dimethylaminopyridine (DMAP), triethylamine (TEA), 2-bromopropionyl bromide, styrene, pentamethyldiethylenetriamine (PMDETA), and Cu(I)Br were purchased from commercial sources. NMR spectra were recorded on a Bruker AV300 MHz and AV500 MHz spectrometers, using CDCl\textsubscript{3} as the solvent. Analytical GPC measurements were performed using a Viscotek GPC system equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2 × PLGel Mix-C and 1 × ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. Further morphological and bulk characterizations were carried out by transmission electron microscope (TEM) (Philips, CM 12) operating at an accelerating voltage of 100 kV. The tapping mode AFM images were taken using a multimode microscope with a NanoScope IIIa Controller (Nanoscope IIIa, Veeco, USA). The UV/Vis measurements were carried out on a Lambda 20 double beam UV/Vis-spectrophotometer from Perkin-Elmer.

2.4.2 Synthesis Details

Naphthyridine-Based ATRP Initiator: To a solution of naphthyridine-OH\textsuperscript{19} (0.67 g, 1.86 mmol), TEA (0.5 mL, 3.7 mmol), and THF (15 mL) was added 2-bromopropionyl bromide (0.78 g, 2.6 mmol) dropwise at 0 °C. The reaction mixture was allowed to stir at 25 °C for 16 h. THF was evaporated and the crude reaction mixture was dissolved in DCM (100 mL) and washed with aq. NaHCO\textsubscript{3} solution. The organic layer was dried over MgSO\textsubscript{4}, concentrated, and purified by column chromatography (Heptane/EtOAc; 80:20) to afford 0.73 g of naphthyridine-based initiator as a white solid (Yield = 77%). \textsuperscript{1}H-NMR (δ, ppm, 300 MHz, CDCl\textsubscript{3}): 9.77
(br, NH), 9.08 (br, NH), 8.59 (d, J = 9 Hz, Ar-H), 8.47 (d, J = 8 Hz, Ar-H), 8.19 (d, J = 9 Hz, Ar-H), 8.16 (d, J = 8 Hz, Ar-H), 5.71 (q, J = 7 Hz, COCHOCO), 2.38 (m, COCH), 2.10 (s, CCH₃), 2.07 (s, CCH₃), 1.75 (m, CCH₂), 1.69 (d, J = 7 Hz, CCH₃), 1.58 (m, CCH₂), 1.36 (m, CCH₂), 1.01 (t, J = 7 Hz, CH₃), 0.89 (br, CH₃); ^13C-NMR (δ, ppm, 75 MHz, CDCl₃): 175.93, 172.28, 169.49, 153.49, 148.09, 139.20, 118.56, 114.19, 71.76, 54.98, 46.84, 32.39, 30.75, 30.61, 29.70, 22.75, 17.53, 13.95, 11.64; ESI-MS: m/z = 507.16 [M+H]^+ (calcd. 506.15 for C₂₃H₃₂BrN₄O₄).

Polystyrene 1: Naphthyridine-based ATRP initiator (650 mg, 1.28 mmol), styrene (20 g, 0.19 mol), PMDETA (44 mg, 2.5 mmol), and Cu(I)Br (184 mg, 1.28 mmol) were taken in a Schlenk tube and degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred under N₂ atmosphere at 80 °C for 20 h. The polymerization mixture was then precipitated into methanol and the precipitate collected was dissolved in a minimum amount of DCM and passed through a silica gel plug to give 4.3 g of naphthyridine end-functionalized PS, 1, as a white powder. ^1H-NMR (δ, ppm, 300 MHz, CDCl₃): 8.58-8.08 (br, Ar-H end-group), 7.33-6.26 (br, Ar-H back-bone), 4.49 (br, COCHOCO), 2.33-0.8 (br, CH₂CH back-bone; and aliphatic-CH from the end group). GPC (CHCl₃): Mₙ = 13100 g.mol⁻¹, Mₕ = 14600 g.mol⁻¹, PDI (Mₕ/Mₙ) = 1.11.

Guanosine End-Functionalized PEG, 2: To a solution of guanosine acid (1.0 g, 1.9 mmol), EDCI.HCl (0.6 g, 2.9 mmol), HOBt (0.39 g, 2.9 mmol), DMAP (0.08 g, 0.7 mmol) in pyridine (60 mL) was added polyethylene glycol monomethyl ether (Mₙ = 5000 g.mol⁻¹) (7.3 g, 1.4 mmol) and the resulting reaction mixture was stirred at 25 °C for 24 h. Pyridine was removed under reduced pressure and the crude solid was dissolved in chloroform (200 mL) and washed with water (3 x 20 mL). The organic layer was dried over MgSO₄, concentrated, and purified by column chromatography (DCM/MeOH; 95:5). Further purification was carried out by dissolving the obtained solid in minimum amount of DCM and precipitating it into 500 mL of diethyl ether. The precipitate was then recrystallized from ethanol to yield 3.9 g of the polymer 2 as a white powder (Yield = 48%). ^1H-NMR (δ, ppm, 300 MHz, CDCl₃): 11.82 (br s,
NH), 8.95 (br s, NH), 7.74 (s, Ar-CH), 6.69 (br s, NH), 5.99 (s, Ribose-CH), 5.20 (br, Ribose-CH), 4.96 (br, Ribose-CH), 4.59 (m, Ribose-CH), 4.48 (m, COOCH₂), 4.23 (m, COOCH₂), 3.89 (br, OCH₂), 3.81-3.47 (br, CH₂CH₂O), 3.40 (m, CH₂OCH₃), 3.29 (m, NHCH₂), 2.61 (br, OCOCH₂CH₂OCO), 1.61 (s, Ribose-CH₃), 1.55 (m, CH₂), 1.39 (s, Ribose-CH₃), 0.96 (t, J = 7.4 Hz, CH₃). GPC (CHCl₃): $M_n = 4200 \text{ g.mol}^{-1}, M_w = 5000 \text{ g.mol}^{-1}, \text{PDI} (M_w/M_n) = 1.19.$

Guanosine End-Functionalized Polyisoprene, 3: To a solution of guanosine acid (0.15 g, 0.28 mmol), EDCI.HCl (0.059 g, 0.28 mmol), HOBt (0.039 g, 0.28 mmol), DMAP (0.005 g, 0.73 mmol) in pyridine (15 mL) was added hydroxyl terminated polyisoprene ($M_n = 6500$) (1.0 g, 0.14 mmol) and the resulting reaction mixture was stirred at 25 °C for 48 h. Pyridine was removed under reduced pressure and the crude solid was purified by column chromatography (DCM/MeOH; 98:2) to yield 0.375 g of the polymer 3 (Yield = 40%). $^1$H-NMR (δ, ppm, 300 MHz, CDCl₃): 12.10 (br s, NH), 9.01 (br s, NH), 7.70 (s, Ar-CH), 5.98 (s, Ribose-CH), 5.25-4.95 (br, =CH), 4.9-4.6 (m, =CH₂), 4.46 (br, Ribose-CH), 4.05 (m, COOCH₂), 3.31 (br, NHCH₂), 2.74 (br, OCOCH₂CH₂OCO), 2.17-1.87 (br, C-CH₂), 1.76-1.52 (br, -CH₃), 1.35 (m, Ribose-CH₃), 0.96 (m, CH₂CH₃). GPC (CHCl₃): $M_n = 5500 \text{ g.mol}^{-1}, M_w = 6600 \text{ g.mol}^{-1}, \text{PDI} (M_w/M_n) = 1.20.$

Formation of Supramolecular Diblock Copolymers and Preparation of the TEM Samples: Polymer 1 and 2 or 1 and 3 were dissolved in toluene in a 1:1 molar ratio (1.5wt% solution) and stirred at room temperature for 72 h. After which the solvent was allowed to evaporate slowly under nitrogen purge at room temperature to yield diblock copolymers 4 or 5 as sticky flakes. These flakes were cryo-sectioned at -60 °C on a Leica Ultracut UCT ultramicrotome to give ~50 nm thick slices. These slices were collected on 600-mesh copper grids. Supramolecular PS-s-PEG (4) diblock copolymer sample was stained with RuO₄ (15 minutes) and PS-s-PI (5) was stained with OsO₄ (6 hours).

Preparation of the Thin Films for AFM Analysis: A 1.5 wt% solution of supramolecular diblock copolymer 4 or 5 in toluene was spin coated onto a silicon
wafer to yield ~100 nm thick films. These as cast films from 4 or 5 were then used for morphology studies. In the case of covalent diblock copolymer, the thin films were annealed under high humidity conditions as described in reference 24.
2.5 References


30. Due to sensitivity of the hydrogen bonding interactions to the humid conditions that are necessary to produce long-range order via solvent annealing process, non-annealed thin film of supramolecular diblock copolymer is compared with solvent annealed covalent diblock copolymer film.
Chapter 3: Synthesis and Thin Film Assembly of Dynamic Covalent Diblock Copolymers

In this chapter, we describe development of a synthetic route to amphiphilic block copolymers connected via a dynamic covalent oxy-imine linkage. This copolymer self-assembles into nanostructured cylindrical morphology in thin films. Removal of the nanosized cylinders by breaking the reversible linkage then afford nanoporous membranes featuring a chemically reactive functionality in the pores. This reactive group can be altered chemically under ambient conditions to furnish pore-functionalized membranes.

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3.1 Introduction

Block copolymer self-assembly\(^1\) has shown remarkable potential towards preparation of highly ordered nanoporous membranes.\(^2\)\(^-\)\(^4\) In this approach, covalently connected yet chemically dissimilar polymer blocks phase separate into ordered nanostructures with length scales on the order of ten to a hundred nanometres. Selective removal of the minor phase from these nanostructured polymer thin films affords nanoporous membranes. Such membranes have found use in surface patterning, templated nanomaterial synthesis, separation, filtration, catalysis, sensing,
and drug delivery applications.\textsuperscript{2,3,5} The far-ranging applicability and performance of these porous materials will be further enhanced if the surface of the nanopore can carry chemically reactive functionalities that can be altered under ambient conditions.\textsuperscript{6} Hillmyer and coworkers have elegantly demonstrated the use of triblock copolymers to create pore-functionalized polymer monoliths.\textsuperscript{7} Russell and Thayumanavan utilized dithiol-linked block copolymers for the preparation of gold functionalized nanoporous thin films.\textsuperscript{4b} However, strategies for covalent chemical functionalization of the nanopores in highly ordered porous thin films remains undeveloped. To this end, in this chapter, we designed a diblock copolymer featuring incompatible blocks, asymmetric block lengths, and a reversible copolymer linkage (Figure 3.1). Self-assembly of this copolymer results in nanostructured thin films exhibiting highly ordered cylindrical morphology. Removal of the nanosized cylinders by reversing the dynamic covalent – oxy-imine – linkage then affords ordered nanoporous membranes that contain chemically reactive oxy-amine functionalities within the pores. Covalent and non-covalent functionalization can then be carried out by reforming imine bonds with fluorescent organic molecules and by generating gold nanoparticle complexes inside of the nanopores.

\textbf{Figure 3.1.} Schematic representation of nanostructured thin film formation from dynamic covalent diblock copolymer, subsequent step of pore formation due to the reversibility of the copolymer linkage, and tentative graphic representation of the functionalized-pore.
3.2 Results and Discussion

3.2.1 Molecular Design and Synthesis

The idea of using a reversible copolymer linkage as a central element in our design is inspired by the work of Lehn. In an impressive body of work, Lehn has beautifully demonstrated that dynamic covalent bonds allow for the preparation of a variety of responsive and adaptive polymeric materials. Like supramolecular interactions, dynamic covalent bonds can be formed and broken under mild conditions. On the other hand, these bonds are more stable than supramolecular contacts. For example, an oxy-imine derivative – the product of a reaction between oxy-amine and aldehyde functional groups – is stable to a variety of chemical manipulations and chromatographic purifications, yet the imine linkage in such compounds can be reversed under certain experimental conditions (pH, temperature, solvent). In the present context, we hypothesized that the stability of the dynamic covalent bond will allow us for a) synthesis and purification of block copolymers linked via a reversible linkage, b) thin film preparation, c) thin film annealing under humid conditions, and d) attaining nanostructured morphology with long-range lateral
order, while the bond reversibility will warrant complete removal of the minor polymer phase and generation of porosity in the thin films. Additionally, reversal of the dynamic imine bond and removal of the generated homopolymer (minor polymer phase) from the thin polymer film will leave behind one of the oxy-imine precursors – either oxy-amine or aldehyde – at the pore surface available for further chemical operations (Figure 3.1).

To test the feasibility of this concept, we decided to utilize a block copolymer composed of poly(ethylene glycol) (PEG) and poly(styrene) (PS) segments connected via an oxy-imine linkage. Preparation of this copolymer was first attempted by coupling oxy-amine end-functionalized PS with aldehyde end-functionalized PEG polymers. However, complete conversion of the homopolymers to the diblock copolymer was not observed. This may have been due to the polymeric nature of the two reactants. Hence, an alternative synthetic pathway was developed in which the oxy-imine contact was established at the PEG chain-end by reacting a small molecule, 1, and polymeric PEG-aldehyde, 2 (Scheme 3.1).

![Figure 3.2](image-url)  
*Figure 3.2. GPC profiles of imine-linked PEG-PS block copolymer and PEG macro-initiator.*
Chapter 3

Figure 3.3. $^1$H-NMR spectra of imine-functionalized PEG-PS block copolymer (top) and PEG macroinitiator (bottom). Solvent peak is marked with an asterisk.

This reaction was found to be complete in a few minutes via ultrasonication and afforded PEG-based macroinitiator 3 ($M_n = 5 \text{ kg.mol}^{-1}$, $M_w/M_n = 1.02$). Macroinitiator 3 was then used to polymerize styrene via an atom transfer radical polymerization (ATRP) process. This procedure yielded the desired block copolymer 4 (PEG-PS, $M_n = 20 \text{ kg.mol}^{-1}$, $M_w/M_n = 1.10$) (Figure 3.2). $^1$H-NMR spectroscopy and size exclusion chromatography (SEC) techniques confirmed block copolymer formation. $^1$H-NMR also confirmed the stability of the oxy-amine linkage towards the ATRP process, as the signal from the imine proton (8.24 ppm) remained unchanged after block copolymerization (Figure 3.3). This synthesis provides a general route towards preparation of PEG-based, high molecular weight, dynamic block copolymers that cannot be prepared by polymer-polymer coupling reaction.

3.2.2 Thin Film Study
Thin films (~50 nm) of diblock copolymer 4 were prepared by spin coating from a toluene solution (1 wt%) onto a silicon substrate. Subsequent solvent annealing under controlled humidity conditions, as demonstrated by Russell and coworkers,\textsuperscript{12} gave rise to a polymer film with self-organized and hexagonally packed arrays of cylindrical PEG-domains (20-25 nm) dispersed in a continuous PS phase with a high degree of long-range lateral order (Figure 3.4a and 3.4b). The nanostructured thin film was then immersed in trifluoroacetic acid (TFA) solution and
then transferred to a water bath. This treatment resulted in breakage of the imine linkages at the interface of the two polymeric domains and solubilizing of the PEG chains by TFA and water. Thus, a nanoporous film was created upon removal of PEG cylinders from the continuous PS matrix. This was evidenced by a clear contrast between the pores and the polymer matrix in SEM as well as TEM imaging (Figure 3.4c and 3.4d).

![IR spectra of the thin film before (solid line) and after (dashed line) PEG removal.](image)

**Figure 3.5.** IR spectra of the thin film before (solid line) and after (dashed line) PEG removal.

IR spectroscopy further supported this conclusion as the typical stretch from the PEG backbone at 1100 cm$^{-1}$ (C-O-C) drastically reduced in intensity after the TFA and water bath treatment of the film (Figure 3.5). Remarkably, the hexagonal order was preserved after the porosity generation.
Figure 3.6. Fluorescence optical microscopy images of dye 5 (a, b and c), and dye 6 (d, e and f), under bright field, mode I, and mode II, respectively. Nanoporous thin film before treatment (g) and after treatment with a 1:1 mixture of 5 and 6 and extensive washing, under mode I (h), and mode II (i).

Figure 3.7. $^1$H-NMR of pyrene-3-aldehyde (top) the porous polymer thin film after functionalization with pyrene aldehyde (bottom).

In order to investigate the availability of the oxy-amine group for further
chemical functionalization, the thin film was immersed in a dimethyl sulfoxide (DMSO) solution containing a 1:1 mixture of a porphyrin molecule, 5, and pyrene aldehyde, 6 (Figure 3.6). Pyrene aldehyde is blue-fluorescent upon excitation at 365 nm (mode I) and non-fluorescent at $\lambda_{ex}$ 546 nm (mode II). In contrast, the porphyrin is red-fluorescent under mode II and non-fluorescent under mode I. Pyrene aldehyde is capable of forming an oxy-imine linkage through its aldehyde group whereas porphyrin is unreactive towards pore oxy-amine functionalities. After exposure to the dye molecules, the film was washed extensively with DMSO to remove any physically adsorbed dyes, and observed under an optical fluorescence microscope. The film exhibited blue fluorescence and was visible under mode I. This suggested that pyrene aldehyde, 6, was chemically bound to the porous film. The film remained optically silent under mode II, at which the red dye is active, suggesting that 5 could not anchor itself to the porous film due to the lack of an amine-reactive functionality and was consequently washed away. This set of experiments indicated availability of the reactive amine groups of the film to the molecules capable of forming a covalent bond. It should be noted that such optical spectroscopy method does not allow for investigations into the nature of the nanopore-wall but confirms only that the films are reactive only to a dye molecule that presents a complementary reactive site. The reason to believe that the functionalization is occurring on the pore-wall is the fact that the copolymer linkage resides at the interface of the two polymer chains. Hence, removal of one polymer chain leaves behind the reactive sites on the newly generated air-polymer interface.

To further evaluate the covalent nature of the film functionalization by 6, the thin film was dissolved in deuterated chloroform and analysed by $^1$H-NMR spectroscopy (Figure 3.7). The spectrum of the polymer showed the typical polystyrene signals (6.3-7.5 ppm) as well as aromatic proton signals from mono-substituted pyrene at 8-8.5 and 9.5 ppm. Absence of the aldehyde proton peak suggested that the sample was not a physical mixture of polystyrene and 6. Area integration analysis suggested that the extent of functionalization was only 50-60%. This suggests that many reactive groups are perhaps imbedded in the polystyrene
matrix and not available for functionalization.

**Figure 3.8.** UV-Vis spectra of the porous polymer thin film after functionalization with pyrene aldehyde.

**Figure 3.9.** Fluorescence spectra of the porous polymer thin film after functionalization with pyrene aldehyde.

UV-Vis and fluorescence emission spectroscopy on the dissolved functionalized membrane corroborated the $^1$H-NMR results by showing typical absorption and emission signals from substituted pyrene system (Figure 3.8 and
Figure 3.9. The post-functionalization reactions occurred at room temperature without the need of any reagents. We then examined the possibility of removing the pyrene molecules from the thin film by reversing the imine linkage under acidic conditions. This resulted in films exhibiting drastic reduction in the fluorescence intensity indicating partial removal of the covalently anchored pyrene molecules under un-optimized conditions (Figure 3.10).

![Figure 3.10](image)

**Figure 3.10.** Decrease in emission intensity after partial removal of pyrene from the thin film.

### 3.3 Conclusions

To summarize, we developed a versatile synthetic route to amphiphilic block copolymers connected via a dynamic covalent oxy-imine linkage. This dynamic copolymer self-assembles into nanostructured cylindrical morphology in thin films. Reversing of the oxy-imine bond under acidic conditions then allowed for removal of the generated PEG homopolymer and creation of oxy-amine functionalized pores in the PS matrix. Covalent film-functionalization was carried out by re-establishing imine bonds to the oxy-amine pore-functionality. Compared to the hydrogen-bonding-based system presented in the last chapter, the present system does allow for formation of highly ordered and reactive membranes. However, this system requires harsh conditions for generation of porosity. The next chapter addresses this precise issue.

### 3.4 Experimental Details
3.4.1 General Methods and Materials

4-carboxybenzaldehyde, polyethylene glycol monomethyl ether \( (M_n = 5000) \), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride \( (EDCI.HCl) \), 1-hydroxybenzotriazole \( (HOBt) \), 4-dimethylaminopyridine \( (DMAP) \), p-xylene glycol, 2-bromoisobutyryl bromide, 2-(tert-butyloxy carbonylaminoxy)acetic acid, \( N,N' \) -dicyclohexylcarbodiimide \( (DCC) \), styrene, Cu(I)Br and pentamethyldiethylenetriamine \( (PMDETA) \) were purchased from commercial sources. NMR spectra were recorded on a Bruker AV300 MHz and AV500 MHz spectrometers, using CDCl\(_3\) as the solvent. Mass spectrometry analyses were performed using an electron ionization (EI) MS spectrometer (Micromass AutoSpec-Ultima). MALDI-TOF mass spectra (matrix: DCTB) were recorded on a Bruker UltraFlex II MALDI-TOF mass spectrometer. Analytical GPC measurements were performed using a Viscotek GPC system equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. IR spectra were recorded using a Bruker Tensor 27 ATR-FT-IR spectrometer (Bruker Optic GmbH, Vienna, Austria). Top-view microstructures of the thin films were characterized using scanning electron microscopy (FEG-SEM, Zeiss LEO Gemini 1530, Germany) with an in-lens detector. Prior to imaging, the thin films were coated with platinum in order to avoid charging and to allow imaging at higher resolutions. Further morphological and structural characterization was carried out by transmission electron microscope (TEM) (Philips, CM 12) operating at an accelerating voltage of 100 kV. The tapping mode AFM images were taken using a multimode microscope with a NanoScope IIIa Controller (Nanoscope IIIa, Veeco, USA). Fluorescent dye functionalized thin films were observed using a fluorescence microscope AX10 Imager M1m (Zeiss, Germany). Images were taken with a low light-intensity CCD camera (PentaMax 12 bit CCD; Princeton Instrument Inc., Trenton, NJ). Zeiss filter set No. 49 was used under mode-I and Zeiss filter set No. 15
was used under mode-II. The UV/Vis measurements were carried out on a Lambda 20 double beam UV/Vis-spectrophotometer from Perkin-Elmer.

3.4.2 Synthesis Details

**Thin Film Studies:** 1 wt% toluene solution of the diblock copolymer, 4, was spin coated on a silicon wafer and the resulting thin film was placed in a glass petri dish with two holes on the lid and a water circulation circuit around the container. Two small containers with wide openings, containing benzene (~5 mL) and water (~2 mL), were placed inside the petri dish and the whole system was cooled to 15 °C. The cooled petri dish was then placed in a Teflon chamber with controlled humidity (>90%). This way the annealing was carried out for a period of 3 days. During this period, the benzene container was refilled three times via a syringe. After this, the petri dish lid was removed and the film was exposed to high humidity conditions for few minutes before removal from the Teflon chamber. After annealing, the thin films were transferred to a TFA bath set at 50 °C for 3 days (Alternatively, 6 days at room temperature produced similar results). Once removed from TFA bath, the films were quickly washed thoroughly with DMSO and ethanol and then immediately put into a water bath for 3h. After this treatment, the films floated on the water surface and were gently transferred onto a TEM grid.

**Postfunctionalization Reactions:** After TFA treatment, the films were washed with water after some time delay. This was important in keeping the films attached to the substrate. These samples were immersed in DMSO (EtOH for fluorescein) in the presence of the respective dye molecule for 18 hours. The films were then washed extensively with DMSO and EtOH to remove any physically adsorbed dye molecules. For functionalization with gold, similar films attached to the substrate were used in conjunction with the procedure described in reference 4b of the main manuscript. In this case, HF bath was used to detach the film from silicon substrate and to transfer the film to the TEM grid.
**Compound 1:** Hydroxy-functionalized ATRP initiator, 1, was synthesized following the literature procedure.\(^1\) \(^1\)H-NMR (δ, ppm, 300 MHz, CDCl\(_3\)): 1.95 (s, 6H, (CH\(_3\))\(_2\)Br), 4.70 (s, 2H, ArCH\(_2\)OH), 5.20 (s, 2H, CH\(_2\)ArCH\(_2\)OH), 7.38 (s, 4H, Ar); \(^1^3\)C-NMR (δ, ppm, 75 MHz, CDCl\(_3\)): 31.0, 55.9, 65.0, 67.3, 127.4, 128.4, 134.9, 141.4, 171.8; ESI-MS: \(m/z = 304.05 \quad [M+NH_4]^+ \) (calcd. 286.02 for C\(_{12}\)H\(_{15}\)BrO\(_3\)); Elemental analysis (%) calcd: C: 50.19, H: 5.26, O: 16.72, Br: 27.83; found: C: 50.13, H: 5.29, O: 16.9, Br: 27.73.

**Compound 2:** Hydroxy-functionalized ATRP initiator 1 (1.0 g, 3.5 mmol), 2-(tert-butyloxy carbonylaminoxy)acetic acid (0.8 g, 1.2 mmol), DCC (1.07 g, 5.1 mmol) and DMAP (0.063 g, 0.5 mmol) were taken in 15 mL of DCM and CH\(_3\)CN mixture (in 2:1 v/v) and the resulting reaction mixture was stirred at 25 °C for 20 h. After the reaction was complete, solvents were removed under reduced pressure and the crude solid was dissolved into a minimum amount of DCM and then filtered. The filtrate was concentrated and purified by column chromatography (heptane/ethyl acetate; 9:1) to yield 1.0 g of compound 2 (Yield = 63%). \(^1\)H-NMR (δ, ppm, 300 MHz, CDCl\(_3\)): 1.46 (s, 9H, (CH\(_3\))\(_3\)), 1.95 (s, 6H, (CH\(_3\))\(_2\)Br), 4.48 (s, 2H, NHOCH\(_2\)), 5.21 (s, 4H, CH\(_2\)ArCH\(_2\)), 7.38 (s, 4H, Ar), 7.74 (s, 1H, NH); \(^1^3\)C-NMR (δ, ppm, 75 MHz, CDCl\(_3\)): 28.4, 31.0, 55.9, 66.8, 67.4, 72.8, 82.4, 128.4, 128.9, 135.4, 136.2, 156.5, 169.7, 171.7; ESI-MS: \(m/z = 477.12 \quad [M+NH_4]^+ \) (calcd. 459.09 for C\(_{19}\)H\(_{26}\)BrNO\(_7\)); Elemental analysis (%) calcd: C: 49.58, H: 5.66, N: 3.04, O: 24.33, Br: 17.36; found: C: 49.28, H: 5.67, N: 3.08, O: 24.23, Br: 17.06.

**Oxy-Imine, 3:** To a solution of compound 2 (0.8 g, 1.7 mmol) in dry DCM (10 mL), TFA (10 mL) was added and stirred for 12 h at 25 °C. After the reaction was over, an aqueous solution of NaHCO\(_3\) was added to it and stirred for 30 min, then the reaction mixture was extracted with DCM, dried over MgSO\(_4\) and the solvent was removed to obtain 0.53 g of compound 3 (Yield = 85%). \(^1\)H-NMR (δ, ppm, 300 MHz, CDCl\(_3\)): 1.95 (s, 6H, (CH\(_3\))\(_2\)Br), 4.29 (s, 2H, CH\(_2\)ONH\(_2\)), 5.21 (s, 4H, CH\(_2\)ArCH\(_2\)), 7.38 (s, 4H, Ar), \(^1^3\)C-NMR (δ, ppm, 75 MHz, CDCl\(_3\)): 31.0, 55.9, 66.3, 67.5, 70.3, 128.4, 128.7, 135.8, 136.1, 170.6, 171.8; ESI-MS: \(m/z = 360.04 \quad [M+H]^+ \) (calcd. 359.04 for...
C_{14}H_{18}BrNO_5); Elemental analysis (%) calcd: C: 46.68, H: 5.04, N: 3.89, O: 22.21, Br: 22.18; found: C: 46.58, H: 5.07, N: 3.76, O: 22.16, Br: 22.20.

**PEG Aldehyde, 4:** To a solution of polyethylene glycol monomethyl ether ($M_n = 5000$ g.mol$^{-1}$) (5.0 g, 1.0 mmol) in 15 mL of pyridine, 4-carboxybenzaldehyde (0.195 g, 1.3 mmol), EDCI.HCl (0.411 g, 2.0 mmol), HOBt (0.270 g, 2.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added and the resulting reaction mixture was stirred at 50 °C for 72 h. Pyridine was removed under reduced pressure and the crude solid was dissolved into a minimum amount of DCM and then precipitated into 200 mL of diethyl ether. The precipitate was filtered and the solid was purified by column chromatography (DCM/MeOH; 9.5:0.5) to yield 4.7 g of 1 (Yield = 91%).

**1H-NMR (δ, ppm, 300 MHz, CDCl$_3$):** 3.35-3.45 (m, CH$_3$(OCH$_2$CH$_2$)$_n$OCH$_2$CH$_2$OCO ArCHO), 3.51-3.77 (br m, CH$_3$(OCH$_2$CH$_2$)$_n$OCH$_2$CH$_2$OCO ArCHO), 3.81-3.93 (m, CH$_3$(OCH$_2$CH$_2$)$_n$OCH$_2$CH$_2$OCO ArCHO), 4.48 (t, 2H, CH$_2$ON=CH), 4.79 (s, 2H, CH$_2$ON=CH), 5.20 (d, J = 9.0 Hz, 4H, CH$_2$ArCH$_2$), 7.37 (s, 4H, CH$_2$ArCH$_2$), 7.62 (d, J = 8.4 Hz, 2H, N=CHAr), 8.04 (d, J = 8.4 Hz, 2H, N=CHAr), 8.24 (s, 1H, N=CH); **13C-NMR (δ, ppm, 125 MHz, CDCl$_3$):** 30.5, 58.9 64.8, 66.1-72.1, 127.3, 128.2, 128.7, 129.9, 130.2, 131.5, 135.8, 135.9,
149.6, 165.7, 171.5, 171.8; GPC (CHCl$_3$): $M_n = 5500$ g.mol$^{-1}$, $M_w = 5600$ g.mol$^{-1}$, PDI ($M_w/M_n$) = 1.02.

**PEG-b-PS, 6:** Macroinitiator 5 (1.0 g, 0.2 mmol), styrene (10.5 g, 0.1 mol), PMDETA (0.07 g, 0.4 mmol), and Cu(I)Br (0.028 g, 0.2 mmol) were taken in a Schlenk tube and degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred under N$_2$ at 110 °C for 20 h. After the reaction was complete, it was cooled to room temperature and then precipitated into hexane for two times. The precipitate was further purified by column chromatography (DCM/MeOH; 30:1) to give 2.3 g of imine-functionalized PEG-b-PS block copolymer. $^1$H-NMR (δ, ppm, 300 MHz, CDCl$_3$): 0.59-2.20 (br m, Br(ArCHCH$_2$)$_m$(CH$_3$)$_2$), 3.37-3.96 (br m, ArCOOCH$_2$CH$_2$O(OCH$_2$CH$_2$)$_n$CH$_3$), 4.48 (t, $J = 4.8$ Hz, ArCOOCH$_2$), 4.79 (s, 2H, CH$_2$ON=CH), 5.20 (br s, 4H, CH$_2$ArCH$_2$), 6.2-7.3 (br m, Br(ArCHCH$_2$)$_m$(CH$_3$)$_2$CCOOCH$_2$Ar) 7.62 (d, $J = 8.1$ Hz, 2H, N=CHAr), 8.04 (d, $J = 7.8$ Hz, 2H, N=CHAr), 8.23 (s, 1H, N=CH); $^{13}$C-NMR (δ, ppm, 125 MHz, CDCl$_3$): 30.0, 40.1-46.7, 59.4 64.6, 66.7-72.2, 125.7-128.8, 130.1, 130.4, 131.1, 131.7, 135.1, 136.1, 137.0, 145.4-146.8, 149.8, 166.2, 169.8, 177.4; GPC (CHCl$_3$): $M_n = 20000$ g.mol$^{-1}$, $M_w = 22000$ g.mol$^{-1}$, PDI ($M_w/M_n$) = 1.10.
3.5 References


Chapter 3


In this chapter, phase-separating polystyrene (PS) and polyethylene glycol (PEG) polymers are connected through a hydrazone-based reversible covalent bond to afford PS-CH=N-PEG diblock copolymer. This dynamic covalent copolymer assembles into a nanostructured cylindrical morphology in thin films. Reversal of the hydrazone linkage and removal of PEG-hydrazide under mild conditions then affords a nanoporous membrane featuring a chemically reactive functionality in the nanopores. Availability of these reactive groups for further thin film functionalization is demonstrated by re-establishing the imine bond with a small molecule amine. This modification strategy does not require any coupling reagent, solvent, or high temperature. Therefore, a gas-phase technique is sufficient for film functionalization purposes.

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4.1 Introduction

Nanoporous thin films with well-defined pore structure and pore properties are useful in the areas of separation, catalysis, water purification, drug delivery, and fuel cell applications.¹ Block copolymer self-assembly² is recognized as one of the
promising routes to generate such porous thin films. In this strategy, chemically
dissimilar segments of a block copolymer are allowed to phase separate into an
ordered structure (such as a hexagonal phase) in thin films. Removal of one polymer
block from the thin film then gives rise to a porous structure. Porous materials created
in this manner display a narrow pore size distribution, uni-directional pore alignment,
high pore density, and tunable pore chemistry. Initially, removal of the polymer
domain was achieved by degradation of the polymer backbone via UV-degradation, reactive ion etching, ozonolysis, and chemical etching methods. Recently,
cleavage of the copolymer junction – rather than the polymer backbone – was shown
to efficiently generate nanoporous thin films. In this approach, only one reaction –
brakeage of the copolymer junction – is required for selective removal of one of the
polymer blocks. Venkataraman and Russell established this concept in thin films by
using an acid-labile trityl linkage in a PS-PEO based phase separating block
copolymer system. Recently, Hawker and coworkers introduced a new family of
acid degradable copolymers featuring an acetal linkage to efficiently fabricate highly
ordered nanoporous membranes. In addition to these chemistries, copolymer
juncture cleavage under redox and UV-irradiation conditions by employing
disulfide/metal chelate and ortho-nitrobenzyl groups, respectively, was
established to yield porous materials. In considering other acid sensitive copolymer
systems, the use of the oxy-imine linkage has proven to give rise to functionalized
porous thin films. However, in all of these systems, use of a reagent is necessary to
bring about the copolymer junction cleavage. Reagents such as trifluoroacetic acid
can be health and environmental hazards. UV irradiation is known to degrade and
crosslink polymers and hence the copolymer cleavage may be associated with
undesired structural and property changes in the polymer thin films. Here, we
demonstrate that careful molecular engineering of the copolymer linkage can give rise
to highly ordered nanoporous thin films in a 2:1 water/methanol solvent mixture at
room temperature (Figure 4.1). An added advantage of this novel system is that the
resulting membranes carry a well-defined reactive moiety in the pores. These reactive
groups can be used for further functionalization of the pore interior. The modification
chemistry employed does not require any coupling reagents or solvents and happen at ambient conditions. Therefore, thin film functionalization can be carried out in the gas phase.

To the best of our knowledge, this work presents the mildest conditions for nanoporosity generation in highly ordered polymer thin films, and their functionalization in solvent-less, reagent-less, and ambient conditions.

4.2 Results and Discussion

4.2.1 Molecular Design and Synthesis

![Figure 4.1. Assembly of a dynamic PS–CH=NH–PEG copolymer into a cylindrical morphology in which the minor polymer block (PEG) forms cylinders in the continuous matrix of the major block (PS). Subsequent removal of PEG–hydrazide gives rise to a PS-based porous matrix decorated with the aldehyde groups that can be subjected to further functionalization step.](image)

In our design, the phase separating polymers, PEG and PS, are connected
through a hydrazone linkage (Scheme 4.1). The stability of the hydrazone bond ensures access to the desired phase separating PEG-N=CH-PS diblock copolymer while the reversibility of the linkage under ambient environment offers opportunity for creating porosity under mild conditions. Moreover, reversal of the hydrazone linkage and removal of one of the components (i.e. PEG-NH$_2$) from the thin film is expected to leave behind the porous matrix decorated with the other hydrazone precursor (i.e. PS-CHO). This reactive group can be used for altering the chemical nature of the pore wall by re-establishing the hydrazone linkage with a desired small molecule amine.

To prepare PEG-NH=CH-PS copolymer, the hydroxyl end-group of PEG ($M_n = 5$ kg.mol$^{-1}$, $M_w/M_n = 1.02$) was transformed into a hydrazide group in three steps. In the first two steps, a $t$-butyl carbazate unit was installed at the PEG chain-end via a $p$-nitrophenyl chloroformate mediated coupling process as shown in Scheme 4.1.
Removal of the t-butoxycarbonyl group then gave access to hydrazide end-functional PEG.† The hydrazide group of 1 was allowed to react with a small molecule aldehyde, 2, carrying a polymerization initiator site. This reaction afforded PEG-based atom transfer radical polymerization (ATRP) initiator 3 ($M_n = 5 \text{ kg mol}^{-1}$, $M_w/M_n = 1.02$). Macrominitiator 3 was used to polymerize styrene via the ATRP process. This procedure gave the desired block copolymer 4 (PEG-b-PS, $M_n = 20 \text{ kg mol}^{-1}$, $M_w/M_n = 1.10$) featuring a hydrazone linkage between the two phase separating polymer blocks.

![Figure 4.2](image.jpg)

**Figure 4.2.** $^1$H-NMR spectra (CDCl$_3$) of PEG-macroninitiator, 3 (top), and diblock copolymer 4 (bottom). Chloroform, water, and diethylether signals are marked with an asterisk.

The $^1$H-NMR spectrum of the macroninitiator, 3, displayed a hydrazone proton resonance at 7.8 ppm and PEG backbone resonances at 3.4-3.9 ppm (Figure 4.2). Block copolymerization with styrene resulted in the appearance of broad signals at 6.2-7.4 ppm and 1-2.4 ppm belonging to the polystyrene aromatic and aliphatic segments, respectively. Proton resonance signals from the hydrazone linker remained
unchanged, establishing stability of the hydrazone group towards ATRP polymerization. Size exclusion chromatography (SEC) corroborated these results as block copolymerization resulted in a shifting of the elution chromatogram of copolymer 4 to lower retention time (Figure 4.3).

![Figure 4.3. GPC profiles of PEG-macroinitiator, 3, and diblock copolymer, 4.](image)

### 4.2.2 Thin Film Study

To investigate the self-assembly and phase separation properties of the hydrazone-linked diblock copolymer, thin films (~100 nm) of 4 were prepared by spin-coating from a benzene solution (1.5 wt%) onto a silicon substrate. Solvent annealing under controlled humidity conditions, as demonstrated by Russell and coworkers,\(^{22}\) produced polymer film with self-organized and hexagonally packed arrays of cylindrical PEG-domains (~25 nm) dispersed in a continuous PS phase with a high degree of long-range lateral order (Figure 4.4). The average center-to-center distance between two cylinders was calculated to be 39 nm. The nanostructured thin film was then immersed in a water/methanol mixture (2:1) at room temperature for 5 days. This treatment caused breakage of the imine linkages at the interface of the two polymeric domains and solubilizing of the PEG chains by the solvent.\(^{23}\) In this way, a nanoporous film was created upon removal of PEG cylinders from the continuous PS
matrix. TEM as well as SEM imaging (Figure 4.4) confirmed this by showing a clear contrast between the pores and the polymer matrix. This conclusion was also supported by IR spectroscopy, as the typical stretch from the PEG backbone at 1100 cm\(^{-1}\) (C-O-C) diminished in intensity after the water treatment of the film (Figure 4.5). The use of a methanol and water mixture gave the best results. This is most likely due to the increased diffusion of the methanol/water mixture through the hydrophobic polystyrene channels.

**Figure 4.4.** AFM height (upper left) and phase (upper right) images (1 \(\mu\)m \(\times\) 1 \(\mu\)m) of the polymer thin film on a silicon wafer after the solvent annealing process. The inset shows the corresponding Fourier transform. TEM (bottom left, scale bar = 200 nm) and SEM (bottom right, scale bar = 100 nm) images of the thin film after removal of the PEG cylinders.
Figure 4.5. IR spectra of the thin film before (top) and after (bottom) removal of the PEG domains.

Figure 4.6. $^1$H-NMR spectra (CDCl$_3$) of the nanostructured polymer thin film before (top) and after (bottom) water: methanol (2: 1) treatment. Signals from chloroform, dichloromethane, and water are marked with an asterisk.
To quantify the extent of the copolymer cleavage and removal of the PEG domains, the thin films were dissolved in deuterated chloroform and examined with the help of $^1$H-NMR spectroscopy (Figure 4.6). Area integration analysis suggested that >95% of the PEG was removed from the thin films. The presence of the aldehyde proton signal at 10 ppm further suggested that the hydrazone linkage was indeed reversed to PEG-hydrazide, which was removed, and PS-aldehyde, which constituted the porous matrix.

![Experimental set-up of the film functionalization.](image)

To examine the effect of an acid on the present dynamic covalent diblock copolymer system, porosity generation studies were carried out in water containing catalytic amounts of hydrochloric acid ($\text{pH} = 4$). These studies suggested that in the presence of an acid, the process of porosity generation could be accelerated and porous films could be obtained overnight. However, presence of a single aldehyde
signal could not be proved unequivocally.

To investigate the availability of the reactive aldehyde units, the thin film was suspended on a glass frit and subjected to vapours of methylamine in methanol (a digital picture of the set-up is shown in Figure 4.7). After 24 hours of vapour treatment, the film was dried under high vacuum condition for 72 hours and then dissolved in deuterated chloroform and analysed by $^1$H-NMR spectroscopy (Figure 4.8). The signal from the methyl protons shifted from 2.4 ppm (in methylamine) to 3.5 ppm (in film) suggested that free amine had reacted with polymer film and converted into an imine group. Absence of the aldehyde signal at 10 ppm also corroborated these conclusions. To further investigate this aspect, a model reaction was carried out with methylamine and benzaldehyde molecules. This reaction produced the imine product in which the methyl signal could be located at 3.5 ppm (Figure 4.9), demonstrating the accuracy of the $^1$H-NMR peak assignment in the case of the functionalized nanoporous thin film.

![Figure 4.8](image.png)

**Figure 4.8.** $^1$H-NMR of the thin film after functionalization in deuterated chloroform. Prior to NMR analysis, the film was dried under high vacuum conditions for 3 days to remove traces of physically absorbed methanol and methylamine molecules.
Figure 4.9. $^1$H-NMR of methylamine in methanol (top) and the model reaction (bottom).

4.3 Conclusions

To summarize, by strategically placing a reversible covalent hydrazone linkage at a phase-separating copolymer junction, highly ordered nanoporous polymer thin films can be obtained in a water and methanol mixture at ambient conditions. The process of porosity generation is simple and does not require use of any external stimulus or reagents. Moreover, upon reversal of the hydrazone linkage and removal of the PEG-NH$_2$ block, the PS porous matrix features aldehyde functional groups. These reactive groups can be chemically altered in the gas phase by re-establishing the imine linkage with a small molecule amine.

The mild nature of the porosity generation and opportunity for gas phase functionalization indicates a broad applicability of the present design in the preparation of pore-functionalized highly ordered nanoporous materials. Therefore, this system represents advantages not seen in the system described in the third chapter. The issue however is that oxy-imine and hydrazone systems suffer from a low number of reactive groups. Therefore, the next chapter examines a strategy that can still operate upon mild conditions but lead to many reactive sites within the nanopore.
4.4 Experimental Details

4.4.1 General Methods and Materials

Polyethylene glycol monomethyl ether \((M_n = 5000 \text{ g.mol}^{-1})\), 4-nitrophenyl chloroformate \((p\text{-NPC})\), triethylamine, \(N,N\text{-diisopropylethylamine (DIPEA)}\), 4-dimethylaminopyridine \((\text{DMAP})\), tert-butyl carbazate, hydrochloric acid \((\text{HCl, 25\% aqueous solution)}\), 2-bromoisobutyryl bromide, 4-hydroxybenzaldehyde, aniline, styrene, Cu(I)Br, and \(N,N,N',N''\text{-pentamethyldiethylenetriamine (PMDETA)}\), and 40\% methylamine solution in methanol were purchased from commercial sources. Compound 4 was prepared according to the literature procedure (R. Narain, S. P. Armes, Biomacromolecules, 2003, 4, 1746). NMR spectra were recorded on a Bruker AV300 MHz spectrometer, using CDCl\(_3\) as the solvent. Analytical GPC measurements were performed using a Viscotek GPC system equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. IR spectra were recorded using a Bruker Tensor 27 ATR-FT-IR spectrometer (Bruker Optic GmbH, Vienna, Austria). Top-view microstructures of the thin films were characterized using scanning electron microscopy (FEG-SEM, Zeiss LEO Gemini 1530, Germany) with an in-lens detector. Prior to imaging, the thin films were coated with platinum in order to avoid charging and to allow imaging at higher resolutions. Further morphological and structural characterization was carried out by transmission electron microscope \((\text{TEM})\) (Philips, CM 12) operating at an accelerating voltage of 100 kV. The tapping mode AFM images were taken using a multimode microscope with a NanoScope IIIa Controller (Nanoscope IIIa, Veeco, USA). The polymer film thickness was determined by a variable-angle spectroscopic ellipsometer \((\text{VASE})\) (M-2000F, LOT Oriel GmbH, Darmstadt, Germany).

4.4.2 Thin Film Studies

The hydrazone-linked PEG-\textit{b}-PS diblock copolymer was spin coated (3000
rpm) from 1.5 wt% benzene solution onto silicon substrates to yield ~100 nm thick films. The film thickness was determined using ellipsometry technique using silicon wafer as a substrate. After annealing in a benzene (3 mL) and H\textsubscript{2}O (1 mL) atmosphere at 17 °C for 24 h, the thin film was then exposed to relatively high humidity (>90%) for 10 min.

To cleave the PEG block and to create porosity, the PEG-\textit{b}-PS thin films were put into a water/methanol (2:1 vol/vol) bath or alternatively into an acidic water bath containing a few drops of HCl (pH = 4). The bath was agitated gently at room temperature. After this treatment, the films floated off the substrate and were collected on carbon-coated TEM grids.

To functionalize, the thin film + water/methanol mixture was suspended on the fritted filter and the liquid part was drained completely, leaving behind the polymer film on top of the frit. Vapours of methylamine (in methanol) were introduced into the system using house vacuum conditions to create low pressure (Figure 4.7). After 24 hours of the functionalization process, the film was dried under high vacuum conditions for 72 hours and then analysed by 1\textsuperscript{H}-NMR spectroscopy.

4.4.3 Synthesis Details

**Carbonate-Functionalized PEG** (1): Polyethylene glycol monomethyl ether (5.0 g, 1 mmol) and triethylamine (0.3 g, 3 mmol) were dissolved in 50 mL anhydrous DCM at 0 °C, followed by the addition of \( p \)-NPC (0.4 g, 2 mmol). After the addition was completed within ~30 min, the reaction mixture was allowed to warm to the room temperature and stirred for 24 h. After partially removing the solvent, the reaction mixture was precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 4.6 g (92%). 1\textsuperscript{H} NMR (\( \delta \), ppm, 300 MHz, CDCl\textsubscript{3}): 3.37 (m, \( \text{CH}_3 \)), 3.40-3.80 (br, \( \text{CH}_2\text{CH}_2\text{O} \)), 3.87 (t, \( \text{CH}_2 \)), 4.44 (t, \( \text{CH}_2 \)), 7.38 (d, 2H, Ar), 8.26 (d, 2H, Ar). 13\textsuperscript{C}-NMR (\( \delta \), ppm, 125 MHz, CDCl\textsubscript{3}): 59.1, 69.1-72.0, 122.3, 125.9, 145.2, 153.3, 157.7.

**Boc-Protected PEG** (2): To a solution of compound 1 (3 g, 0.6 mmol), \textit{tert}-butyl carbazate (0.63 g, 4.8 mmol), DIPEA (0.39 g, 3 mmol), DMAP (0.04 g, 0.3 mmol),
anhydrous DCM (30 mL) was added and the resulting reaction mixture was stirred at room temperature for 24h. After removing the solvent, the crude product was dissolved in chloroform and thoroughly washed with aq. Brine solution. The organic layer was then dried over MgSO₄, concentrated, and dissolved in a minimum amount of DCM and precipitated into an excess of anhydrous diethyl ether for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 2.6 g (88%). ¹H-NMR (δ, ppm, 300 MHz, CDCl₃): 1.45 (s, CH₃), 3.33 (m, CH₃), 3.40-3.73 (br, CH₂CH₂O), 3.86 (t, CH₂), 4.27 (t, CH₂), 6.61 (br, NH), 6.92 (br, NH). ¹³C-NMR (δ, ppm, 125 MHz, CDCl₃): 18.8, 59.0, 64.6, 66.5, 69.4-71.9, 161.3.

**Hydrazide End-functionalized PEG (3):** Compound 2 (2.0 g, 1 mmol) was dissolved in 10 mL of H₂O at 0 °C, followed by the addition of HCl (2 mL). The reaction mixture was then stirred for 1 h. After removing the solvent, the crude product was dissolved in a mixture of DCM (10 mL) and triethylamine (3 mL) and stirred for another 1 h. The mixture was thoroughly washed with brine. Organic layer was then dried over MgSO₄, concentrated, and dissolved in a minimum amount of DCM and precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 1.7 g (85%). ¹H NMR (δ, ppm, 300 MHz, CDCl₃): 3.37 (m, CH₃), 3.40-4.02 (br, CH₂CH₂O), 4.33 (br, CH₂), 8.84 (br, NH), 10.05 (br, NH). ¹³C-NMR (δ, ppm, 125 MHz, CDCl₃): 59.1, 64.5, 69.3-71.9, 161.3.

**PEG Macroinitiator 5:** Hydrazide end-functionalized PEG 3 (1.0 g, 0.2 mmol) and aldehyde 4 (0.27 g, 1 mmol) were dissolved in 25 mL of chloroform, followed by the addition of aniline (9.3 mg, 0.1 mmol). The reaction mixture was stirred at room temperature for 24 h. After partially removing the solvent, the reaction mixture was precipitated into an excess of anhydrous diethyl ether thrice. The obtained white solids were dried in a vacuum oven overnight at room temperature with a yield of 0.96 g (82%). ¹H NMR (δ, ppm, 300 MHz, CDCl₃): 2.06 (s, CH₃), 3.37 (m, CH₃), 3.40-4.05 (br, CH₂CH₂O), 4.38 (t, CH₂), 7.16 (d, 2H, Ar), 7.76 (d, 2H, Ar), 7.93 (s,
CH), 8.88 (br, NH). $^{13}$C-NMR ($\delta$, ppm, 125 MHz, CDCl$_3$): 30.6, 55.2, 59.0, 61.7, 69.3-71.9, 121.3, 128.4, 132.1, 154.3, 169.9; GPC (CHCl$_3$): $M_n = 5800 \text{ g.mol}^{-1}$, $M_w = 6200 \text{ g.mol}^{-1}$, PDI ($M_w/M_n$) = 1.07.

**PEG-b-PS Dynamic Covalent Block Copolymer 6:** Macroinitiator 5 (0.5 g, 0.1 mmol), styrene (5.2 g, 50 mmol), PMDETA (35 mg, 0.2 mmol), and Cu(I)Br (14.3 mg, 0.1 mmol) were taken in a schlenk tube and degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred under N$_2$ at 110 °C for 5 h. After the reaction was complete, it was cooled to room temperature and then precipitated into hexane for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature with a yield of 1.04 g (18%). $^1$H NMR ($\delta$, ppm, 300 MHz, CDCl$_3$): 0.82-2.37 (br, CH$_2$CH backbone; and $\alpha$-CH from the end group, PS), 3.37 (m, CH$_3$, PEG), 3.40-4.05 (br, CH$_2$CH$_2$O, PEG), 4.40 (t, CH$_2$, PEG), 6.27-7.46 (br, Ar-H backbone, PS), 7.58 (t, 2H, Ar), 7.87 (s, CH), 8.74 (br, NH). GPC (CHCl$_3$): $M_n = 20000 \text{ g.mol}^{-1}$, $M_w = 22000 \text{ g.mol}^{-1}$, PDI ($M_w/M_n$) = 1.10.
4.5 References

1. For an excellent review article, please see: M. Ulbricht, *Polymer*, 2006, 47, 2217.


23. When reversibility of the hydrazone linkage in polymer 4 was examined in solution, the $^1$H-NMR and SEC analyses indicated that the copolymer was intact in pure water and needed catalytic amounts of hydrochloric acid for reversal to its PEG-hydrazide and PS-aldehyde precursors. The amphiphilic diblock copolymer 4 is most likely in a micellar structure in an aqueous solution. Impact of this secondary structure on the hydrolysis of the hydrazone linkage in pure water in solution remains unknown.
Chapter 5: Assembly of Interacting Binary Blends of Diblock Copolymers in Thin Films

In this chapter, self-assembly of a binary mixture of poly(styrene)$_{336}$-block-poly(4-vinyl pyridine)$_{25}$ (PS$_{336}$-b-P4VP$_{25}$) and poly(ethylene glycol)$_{113}$-block-poly(4-hydroxy styrene)$_{25}$ (PEG$_{113}$-b-P4HS$_{25}$) is shown to give rise to a cylindrical morphology in thin films through pyridine/phenol-based heterocomplementary hydrogen bonding interactions between the P4VP and P4HS copolymer segments. Removal of the cylindrical phase (PEG-b-P4HS) allowed access to porous materials having a pore surface decorated with P4VP polymer blocks. These segments could be transformed into cationic polyelectrolytes through quaternization of the pyridine nitrogen atom. The resulting positively charged nanopore surface could recognize negatively charged gold nanoparticles through electrostatics interactions. This chapter, therefore, outlines the utility of supramolecular AB/CD type of block copolymer towards preparation of highly ordered porous thin films carrying a chemically defined channel surface with a large number of reactive sites.

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5.1 Introduction

Block copolymers with incompatible polymer segments are known to self-assemble in thin films and bulk state into a variety of nanostructured morphologies.$^{1-3}$
Typically, copolymers having a purely covalent chemical structure are studied. Of recent, however, copolymer structures stabilized through non-covalent/dynamic interactions are also attracting considerable attention. This is due to the realization that reversibility of supramolecular and dynamic covalent interactions can impart stimuli responsivity and adaptability to the nanostructured polymer thin films. Furthermore, a high degree of achievable molecular complexity in the supramolecular copolymers is expected to give rise to new morphologies. Towards this end, phase separation properties of blends of AB/C, AB/B’C, AB/CD, ABA/CD, ABA/CDC, or ABC/AD types of copolymers in which two blocks carry non-covalent interactions have been studied. Immiscible polymer mixtures bearing non-covalent interactions at either one or both chain ends has also been established. Alternatively, mixing of small molecules capable of interacting with one polymer block is shown to give polymer films containing structural hierarchy.

Our attention is drawn towards an AB/CD system in which B and C polymer blocks are homopolymer sequences designed to communicate with each other through hetero-complementary interactions (Scheme 5.1). This is due to the fact that cylindrical morphology of such binary diblock copolymer blends in thin films can give access to nanoporous membranes upon removal of the cylindrical domains through breaking of the supramolecular interactions between the B and C blocks. In this design, the generated nanopores will carry a polymer brush (B or C segment) on the pore surface. This strategy of accessing pore-functionalized porous thin films has the advantage of having a higher number and higher availability of the reactive sites within the nanopore. Reports on the AB/CD system, however, are restricted to self-assembly studies in the bulk state only. Moreover, no attempts were made to create and examine the nanoporous structures from the assembled materials. To address these deficiencies, in this chapter, we explore: i) synthesis and self-assembly of poly(styrene)-block-poly(4-vinyl pyridine) (PS-b-P4VP) and poly(ethylene glycol)-block-poly(4-hydroxy styrene) (PEG-b-P4HS) diblock copolymers in thin film through hydrogen bonding interactions between the P4HS and P4VP polymer blocks, ii) porous membrane formation through removal of the PEG-b-P4HS block
copolymers from the thin film, iii) chemical ionization of the P4VP polymer brush located on the pore surface, and iv) availability of the cationic P4VP segment for further modification of the nanopores.

5.2 Results and Discussion
5.2.1 Molecular Design and Synthesis

Synthesis of the required PEG-\textit{b}-P4HS copolymer was achieved in two synthetic steps (Scheme 5.2). In the first step, atom transfer radical polymerization (ATRP)\(^{24}\) of acetoxy-styrene monomer by PEG-based macroinitiator 1\textit{a} \((M_n = 4900\text{ g.mol}^{-1}, M_w/M_n = 1.03)\) gave rise to PEG-\textit{b}-PAS diblock copolymer 1\textit{b} \((M_n = 10500\text{ g.mol}^{-1}, M_w/M_n = 1.09)\). Removal of the acetoxy groups by hydrazine led to the formation of PEG\(_{113}\)-\textit{b}-P4HS\(_{25}\) copolymer 1 \((M_n = 8900\text{ g.mol}^{-1}, M_w/M_n = 1.08)\). This sequence of events could be followed by \(^1\text{H}-\text{NMR}\) spectroscopy and gel permeation chromatography (GPC). In \(^1\text{H}-\text{NMR}\) spectroscopy, block copolymerization was evident by the appearance of the proton resonances belonging to the acetoxy and aromatic units at 2.2 and 6-7 ppm, respectively (Figure 5.1).
Figure 5.1. $^1$H-NMR of the macroinitiator 1a (top) and diblock copolymers 1b (middle) and 1 (bottom).

![NMR Spectra](image)

**Figure 5.2.** GPC traces of the macroinitiator 1a and diblock copolymers 1b and 1.

GPC indicated an increase in the hydrodynamic volume of polymer 1b as a result of block copolymerization (Figure 5.2). As expected, removal of the acetoxy groups resulted in a decrease in the hydrodynamic volume of polymer 1. Copolymer 2, PS$_{336}$-b-P4VP$_{25}$ (PS: $M_n = 35000$ g.mol$^{-1}$, P4VP: $M_n = 2700$ g.mol$^{-1}$, $M_w/M_n = 1.09$), was obtained from commercial sources.

### 5.2.2 Thin Film Study

Block copolymers 1 and 2 having similar numbers of complementary non-covalent bonding sites (~ 25) were mixed$^{25}$ in dioxane and a 1wt% solution was used to cast a thin film (~ 60 nm) on a freshly pre-cleaned silicon substrate. The polymer thin film was then subjected to a solvent annealing protocol$^{26}$ under a mixed atmosphere of benzene and methanol vapors.

The morphology of the polymer film after the solvent annealing treatment was examined with the help of atomic force microscopy (AFM) (Figure 5.3a). This surface scan of the polymer thin film suggested that the binary blend of block copolymers phase-separated at the nanometer scale, most likely due to the stabilization through hydrogen bonding interactions between the P4VP and P4HS polymer blocks. AFM images of the polymer surface indicated an apparent hexagonal
cylindrical morphology with average cylinder diameter of ~20 nm. This size is smaller than usually observed in other PEG-based systems. It should be noted, however, that unlike other PEG-based systems, the present system did not use high humidity condition during the solvent annealing protocol and hence the PEG domains were not swollen with water. The hexagonally ordered thin film was then transformed into a porous structure through removal of the PEG-b-P4HS copolymer cylindrical domains. This was achieved by immersing the film in an aqueous NaOH solution. Due to the chemically basic nature of this medium, the phenol groups of the P4HS segment transformed into phenolate anions and could no longer bond with the nitrogen atom of the pyridine group (Scheme 5.1).
Figure 5.3. AFM height (left) and phase (right) images of the self-assembled polymer thin film before (top, a) and after (bottom, b) removal of the cylindrical domains.

Figure 5.4. TEM images of the polymer thin film after removal of the cylindrical domains (without staining), a, and after iodine staining, b.

Moreover, due to high water solubility of the PEG segment, copolymer 1 was solubilized by the aqueous medium. In this way, the thin film became porous due to the breaking of the hydrogen bonding interaction and subsequent solubilization of polymer 1 in water. The porous cylindrical structure was confirmed with the help of AFM, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) analyses. This study also suggested that the order remained upon removal of the cylindrical domains. Although a clear phase change was observed upon removal of the cylindrical domain by AFM (Figure 5.3b), in TEM and SEM, a low contrast was seen (Figure 5.4a and 5.5). This is most likely due to the pores in the present system being not completely empty but rather carrying the P4VP brush-like domain in the nanopores.

Therefore, rather than a clear pore, the present pores are perhaps filled by the loosely packed P4VP segments. To verify this, the film was stained with iodine, which is preferential for the P4VP segment (Figure 5.4b). The cylindrical domain appeared completely dark under this stain, suggesting that the P4VP segment occupied the pores. The pyridine group of the P4VP block was transformed into the
pyridinium cation by reaction with methyl iodide in methanol. These nanoporous membranes were then immersed in an ethanolic solution of negatively charged gold nanoparticles of sizes varying from 0.8-3.5 nm (Figure 5.6). It was envisaged that the positively charged pyridine groups of the polymer thin film would associate with the negatively charged gold nanoparticles through electrostatic interactions. Manners and coworkers have demonstrated this strategy to be an effective protocol for the preparation of polymer cylinders and gold nanocomposites. After the exposure to the nanoparticles, the films were washed thoroughly with deionized water and methanol. This treatment was critical in ensuring that any recognition event within the nanochannels was due to the electrostatic interactions as weaker interactions such as hydrogen bonds are expected to break in polar solvents such as water and methanol.

Figure 5.5. SEM images of the polymer thin film after removal of the cylindrical domains (platinum coating).
Figure 5.6. TEM images of negatively charged gold nanoparticles (top) and the positively charged porous thin film upon interaction with these nanoparticles (bottom).
Scanning electron microscopy (SEM) and TEM techniques were then employed to examine the films before and after interaction with gold nanoparticles (Figure 5.6-5.9). Both techniques suggested that the negatively charged gold nanoparticles were localized within the nanochannels of the thin polymer film and no particles could be found on the polymer matrix. This suggested that their interaction to the pore-wall was due to the electrostatic interactions between the negatively charged inorganic nanoparticle surface and positively charged pyridine group of the P4VP block. To confirm this, a control experiment was carried out. In this experiment, nanoporous thin films that were not subjected to the pyridine-quaternization process were used. Under identical conditions, these films were exposed to gold nanoparticles and then washed with water and methanol and observed with SEM technique. In this case, the gold nanoparticles could not be observed. This suggested that negatively charged gold nanoparticles could not form a strong complex.
with the chemically neutral pyridine groups of the nanopores and consequently washed away upon treatment with water and methanol.

*Figure 5.8. SEM images of the polymer thin film upon complexation with negatively charged gold nanoparticles (without platinum coating).*
Figure 5.9. Zoom-in at one pore of the porous thin film carrying gold nanoparticles, the circle is hand-drawn (top), and the control experiment (without platinum coating) (bottom).

5.3 Conclusions
In conclusion, assembly of $\text{PS}_{336}-b$-$\text{P4VP}_{25}$ and $\text{PEG}_{113}-b$-$\text{P4HS}_{25}$ block copolymers resulted in the formation of nanostructured cylindrical morphology in polymer thin films through hydrogen bonding interactions between the P4VP and P4HS copolymer segments. The cylindrical domains ($\text{PEG}-b$-$\text{P4HS}$) could be removed by breaking the hydrogen bonding interactions in an aqueous medium. This gave rise to a nanoporous thin film carrying P4VP polymer segments on the nanopore wall. This polymer segment could be transformed into a cationic polyelectrolyte through quaternization of the pyridine nitrogen atom. The resulting positively charged pore surface could recognize negatively charged gold nanoparticles through electrostatic interactions. In essence, this chapter demonstrates the utility of the AB/CD type of binary blend of block copolymers in accessing nanoporous thin films of controlled and tunable pore chemistry. Such opportunity for pore-surface modification is expected to lead to nanoporous materials with enhanced separation and filtration properties.

One aspect that could be studied regarding the porous film characterization is the cross-sectional analysis. At the time of submission of this thesis, however, progress in this direction remains limited due to many technical issues. Nonetheless, the efforts are still ongoing.

5.4 Experimental Details

5.4.1 General Methods and Materials

Negatively charged gold nanoparticles were purchased from Nanoprobes (please see Figure 5.6 for TEM from this sample). Poly(styrene)-block-poly(4-vinyl pyridine) ($\text{PS}_{336}-b$-$\text{P4VP}_{25}$) copolymer with a dispersity of 1.09 was purchased from Polymer Source, Inc. Polyethylene glycol monomethyl ether ($\text{PEG}_{5000}$), 4-acetoxy styrene, ethyl 2-bromoisobutyrate, methyl iodide, Cu(I)Br, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), and ammonium hydroxide were purchased from commercial sources. NMR spectra were recorded on a Bruker AV300 MHz spectrometer, using CDCl$_3$ as the solvent. Analytical GPC measurements were
performed using a Viscotek GPC system equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. Top-view microstructures of the thin films were characterized using scanning electron microscopy (FEI Magellan 400) with an in-lens detector (X-sectionanl imaging, 45°). Further morphological and structural characterization was carried out by transmission electron microscope (TEM) (Philips, CM 12) operating at an accelerating voltage of 100 kV. The tapping mode atomic force microscopy (AFM) images were taken using a multimode microscope with a NanoScope IIIa Controller (Nanoscope IIIa, Veeco, USA).

5.4.2 Synthesis Details

**Polymer 1a**: PEG-Br macroinitiator (1 g, 0.2 mmol), 4-acetoxystyrene (2.5 g, 15 mmol), HMTETA (46 mg, 0.2 mmol), and Cu(I)Br (28 mg, 0.2 mmol) were taken in a Schlenk tube and degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred under N\textsubscript{2} at 110 °C for 6 h. After this time, the reaction mixture was cooled to room temperature and then precipitated into hexane for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature to give 1.4 g of the desired diblock copolymer. \textsuperscript{1}H NMR (δ, ppm, 300 MHz, CDCl\textsubscript{3}): 0.82-1.96 (br, CH\textsubscript{2}CH backbone, PAS), 3.37 (m, CH\textsubscript{3}, PAS), 3.36-3.83 (br, CH\textsubscript{3}CH\textsubscript{2}O, PEG), 3.91 (t, CH\textsubscript{2}, PEG), 6.24-7.03 (br, Ar-H backbone, PAS). GPC (DMF): M\textsubscript{n} = 10500 g.mol\textsuperscript{-1}, M\textsubscript{w} = 11100 g.mol\textsuperscript{-1}, PDI (M\textsubscript{w}/M\textsubscript{n}) = 1.09.

**Polymer 1b**: Polymer 1a (1 g, 0.1 mmol) was dissolved in 5 mL of THF at 25 °C, followed by the addition of ammonium hydroxide (0.5 g, 10 mmol). The reaction mixture was then stirred for 12 h. After removing the solvent, the crude product was dissolved in methanol and precipitated into an excess of hexane for three times. The obtained white solid was dried in a vacuum oven overnight at room temperature to give 0.7 g of copolymer 1b. \textsuperscript{1}H NMR (δ, ppm, 300 MHz, D\textsubscript{2}O): 1.04-2.10 (br, CH\textsubscript{2}CH backbone, PAS), 3.51-4.51 (br, CH\textsubscript{3}CH\textsubscript{2}O, PEG), 6.37-7.06 (br, Ar-H
backbone, PAS). GPC (DMF): $M_n = 8900 \text{ g.mol}^{-1}$, $M_w = 9600 \text{ g.mol}^{-1}$, PDI ($M_w/M_n$) = 1.08.

**Preparation of thin films:** A clean silicon substrate was immersed into MeOH and sonicated for 15 minutes and subsequently in acetone for another 15 minutes. After drying under a flow of nitrogen, the silicon substrates were then placed in 50-60% humidity for 12 h. The substrates after cleaning and humidity treatment were immediately used for the spin coating of copolymers. Polymer 2, PS-b-P4VP (8 mg), and polymer 1 (1.5 mg) were dissolved in 0.95 g of 1,4-dioxane and stirred at room temperature for 48 h. The 1 wt% solution of these copolymers was spin coated onto the pre-treated silicon substrate to yield ~ 60 nm thick films. These thin films were annealed in a closed chamber in a benzene (10 mL) and MeOH (2 mL) atmosphere at 17 °C for 24 h. The environment outside the chamber was maintained at < 20% humidity.

**Porosity generation:** To remove the PEG-b-P4HS copolymer from the thin film in order to create nanoporosity, the copolymer thin films were put into DMSO (2 mL)/aq. NaOH (0.1mL, 0.1M) bath. The bath was shaken gently at room temperature for 2 h and the films were washed with methanol for two times. After this treatment, the films floated off the substrate and were collected on carbon-coated TEM grids.

**Au-functionalized thin films:** The nanoporous thin films were put into MeOH (15 mL)/methyl iodide (2mL) bath under shaking at 45 °C for 48 h, and then washed by methanol and water for three times each. After this, the film was immersed into ethanol solution of gold nanoparticles (5 mM) for 12 h at room temperature and then thoroughly rinsed with deionized water and MeOH for several times and then observed with the help of SEM.
References


Chapter 5


22. For an alternative approach based on an AB/C system, please refer to reference 11(d).


The work carried out in this thesis points to the following general conclusions:

1. Replacement of a carbon-carbon covalent bond with a quadruple hydrogen-bonding motif in phase-separating diblock copolymers results in the loss of long-range lateral order and high polydispersity of the cylindrical nanostructures formed in the polymer thin film.

2. Use of dynamic covalent bonds that can be formed and broken under mild conditions presents a good substitute to the hydrogen bonding interactions. In this case, the polymer thin films retain their high lateral order as seen in the case of block copolymers connected through a carbon-carbon covalent bond.

3. Use of a dynamic covalent bond allows for porosity generation as well as nanopore functionalization under mild conditions.

4. The dynamic covalent bond-based systems afford polymer thin films with a low number of available reactive sites within the nanopore.

5. The number of these reactive sites can be increased, while still retaining the mild conditions for porosity formation and pore functionalization, by increasing the number of hydrogen bonding sites at the copolymer junction to about 25.

Therefore, as per the requirement, either a dynamic covalent or multiple hydrogen bonding-based system can be employed for the fabrication of highly ordered porous polymer thin films containing a known and reactive chemical identity in the nano-channels.
## Symbols and Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PI</td>
<td>poly(isoprene)</td>
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<tr>
<td>PBD</td>
<td>poly(butadiene)</td>
</tr>
<tr>
<td>PLA</td>
<td>poly(lactide)</td>
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<td>PEG</td>
<td>poly(ethylene glycol)</td>
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<td>PDMS</td>
<td>poly(dimethylsiloxane)</td>
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<td>PS</td>
<td>poly(styrene)</td>
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<td>ATRP</td>
<td>atom transfer radical polymerization</td>
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<td>trifluoroacetic acid</td>
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<td>AFM</td>
<td>atomic force microscopy</td>
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<td>ultraviolet-visible</td>
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<td>nuclear magnetic resonance</td>
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<td>transmission electron microscope</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
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<td>SEC</td>
<td>size exclusion chromatography</td>
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<td>MALDI-TOF</td>
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<td>PDI</td>
<td>polydispersity index</td>
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<td>DIPEA</td>
<td>$N,N$-diisopropylethylamine</td>
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<td>P4VP</td>
<td>poly(4-vinyl pyridine)</td>
</tr>
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<td>P4HS</td>
<td>poly(4-hydroxy styrene)</td>
</tr>
<tr>
<td>HMTETA</td>
<td>1,1,4,7,10,10-hexamethyltriethylenetetramine</td>
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</table>
Curriculum Vitae

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2013  Chinese Government Award for Outstanding Self-financed Students Abroad
2008  Outstanding Graduate Students in USTC
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Research and Professional Experience

2013  Research mentoring of master and doctoral students
2009-2010 Lab Assistant, Praktikum III, Teaching 3rd semester students, D-MATL, ETH Zürich
2003-2005 Research Assistant, DongMu Insulating Material Co. Ltd.

Skills and Experience

- Several years of experience in organic synthesis and polymer synthesis (RAFT, ATRP, ROP, Polypeptide synthesis, and etc.)
- Experience with Gel permeation chromatography (GPC), Nuclear magnetic resonance (NMR) spectroscopy, Scanning electron microscope (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Microtome, Fluorescence microscopy (FM), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Ultraviolet-visible spectroscopy (UV-Vis), Infrared spectroscopy (IR), X-ray diffraction (XRD), Small-angle X-ray scattering (SAXS), Dynamic and static light scattering, Stopped-flow spectroscopy.

Peer-reviewed publications

Curriculum Vitae

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