Ordered, porous and multifaceted polymer films

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Introduction

Polymeric films with highly ordered pores of narrow size distribution are of great interest to industry for a variety of applications. Methods for the formation of ordered porous polymeric films are currently dominated by 'top down' lithographic techniques that use electrons or high-energy molecules to pattern surfaces. These techniques are complicated and expensive, especially when applied to nanoscaled structures.[1]

In 1994, microporous polymer films were produced by a simple templating technique based on the self-assembly of water droplets known as the 'breath figure' (BF) technique.[2] The films were cast from a volatile solvent under conditions of high humidity onto a flat surface. The cooling caused by solvent evaporation induced condensation of water droplets onto the solution surface. These water micro-spheres self assemble into hexagonally packed arrays. The droplets create a highly ordered template where the polymer can precipitate at the water interface, effectively stabilizing the droplets from coalescence. Ultimately a three dimensional (3D) porous structure is formed, with pores arranged in a hexagonal pitch, see Figure 1 for schematic representation of the process. Polymers capable of forming spherical structures in solution has been shown critical in forming these films.[2] Here, I utilize the "arm first technique"[3] to prepare star polymers known as the core crosslinked star (CCS) polymers (Scheme 1), utilizing atom transfer radical polymerization (ATRP). This technique has the advantage of control of architecture (i.e., number of arms and molecular weight) and functionality (i.e., core, pendant, or end functional). This technique can even be used to prepare star poly(electrolytes) and form multilayered films.[4] Herein, I will demonstrate through careful design of star polymer composition and functionality, porous and three dimensionally conformal materials can be prepared.
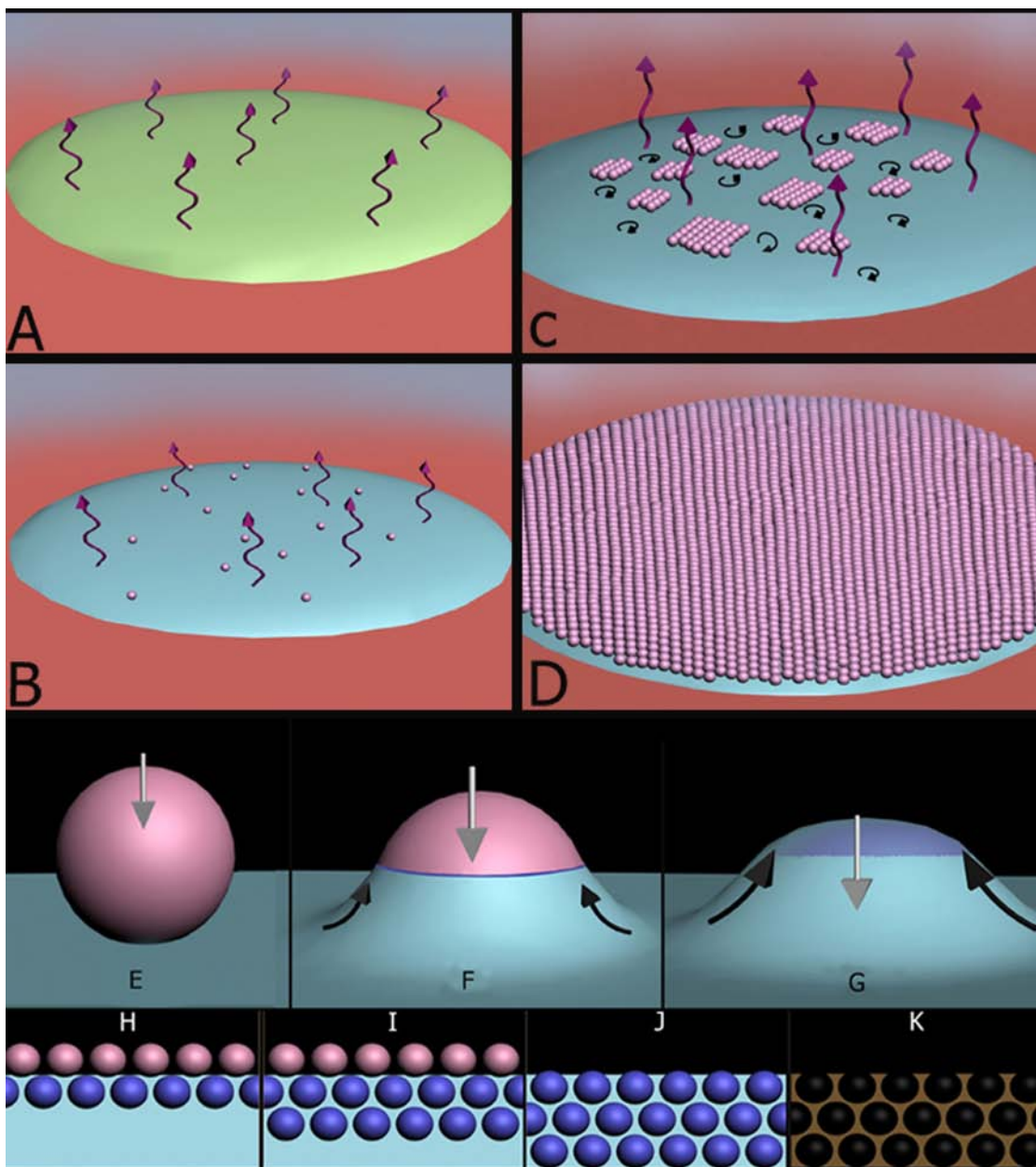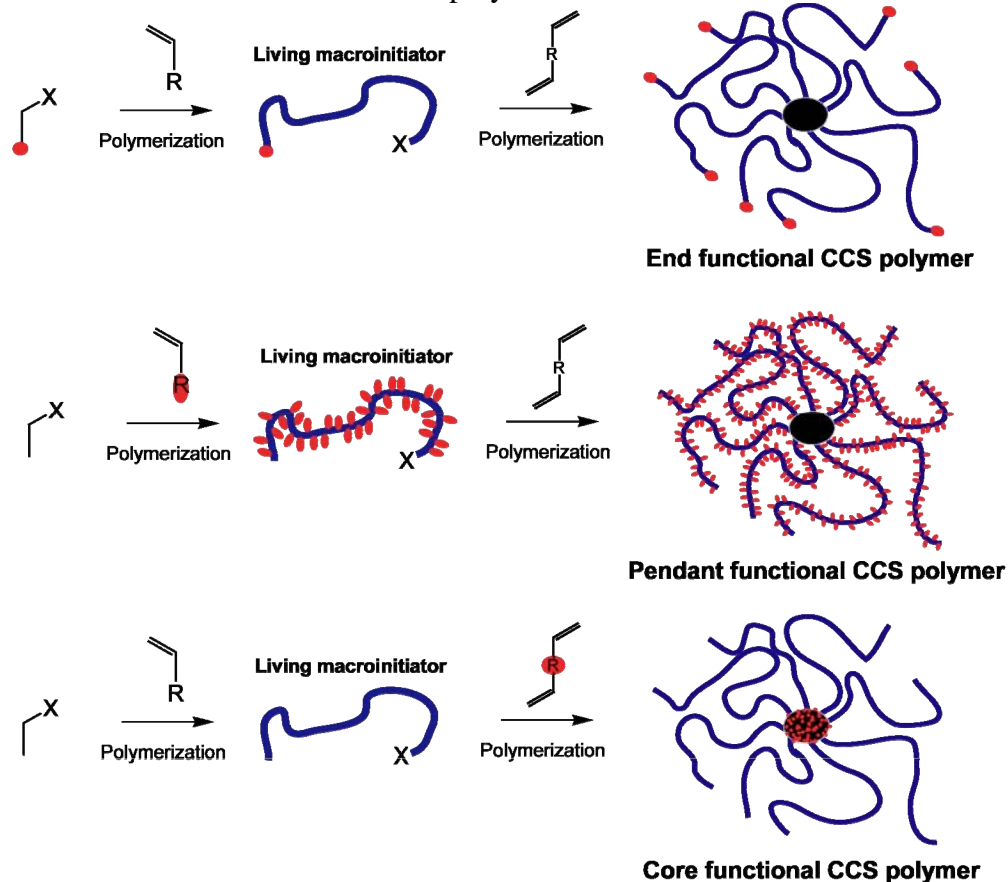
Figure 1. Schematic representation of honeycomb films by the 'breath figure' technique. **(A)** The solvent rapidly evaporates causing an evaporative cooling effect hence the temperature of the solution surface drops. **(B)** The drop in temperature [represented by a colour change from green to blue] initiates the condensation of water droplets known as breath figures. [represented diagrammatically by pink spheres] **(C)** The water micro-spheres stabilize [possibly due to thermo-capillary convection] and self assemble into ordered arrays, [possibly induced by variations in local surface tensions and convection in the liquid layer]. **(D)** The water droplets quickly cover the solution surface in a close packed hexagonal arrangement. **(E,F,G)** The polymer will precipitate at the water interface [represented by dark blue layer]. This solid envelope is pulled over the water droplet by the high surface tension. The solution surface becomes free for more water droplets to condense. **(H,I,J,K)** Another layer of water droplets will repeat this process (A-G). This will continue until all solvent has evaporated. This gives rise to a 3-D structure, consisting of multiple layers of seemingly independent pores, with the top surface displaying an open porous structure.

Scheme 1. Synthesis of star polymers by the arm first technique; initially a controlled polymerization technique is used to prepare a living macroinitiator, then a divinyl monomer is reacted under controlled conditions to ultimately form a core crosslinked star (CCS) polymer. Outlined here are three synthetic strategies to prepare functional CCS-polymers

Living macroinitiator

Polymerization   Polymerization

End functional CCS polymer

Living macroinitiator

Polymerization   Polymerization

Pendant functional CCS polymer

Living macroinitiator

Polymerization   Polymerization

Core functional CCS polymer

Control of porous structure through controlled polymerization

The BF technique has the advantage of facile control of pore size. I detailed the first report using CCS polymers to form highly ordered porous films (Figures 2A to 2D).[5]   It was shown that the pore diameters decrease with increasing number of poly(methyl methacrylate) (PMMA) arms and with increasing molecular weight of the star polymer (Figure 2e and 2f).
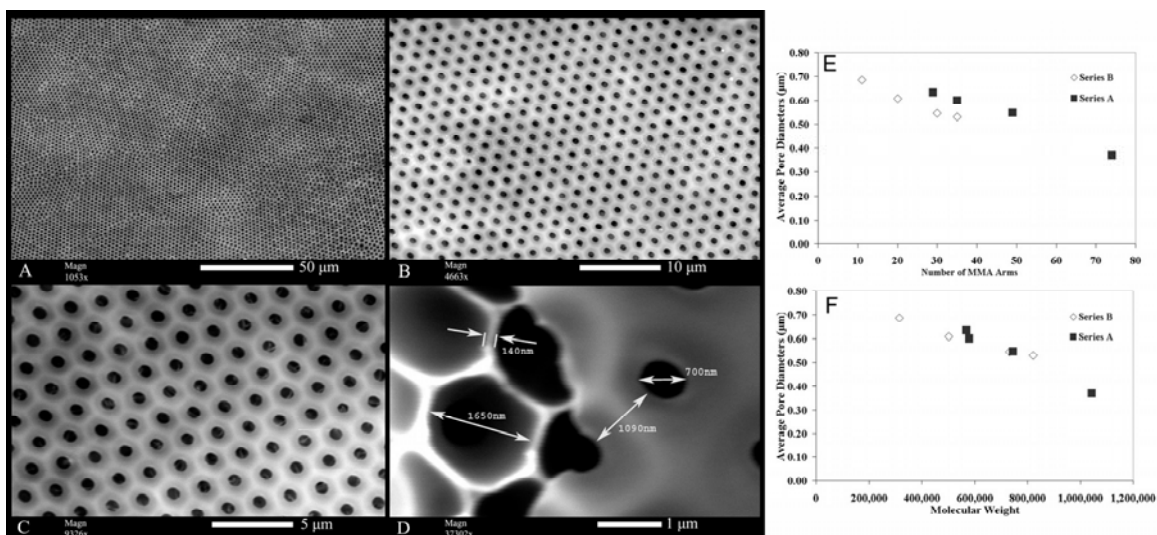
Figure 2- Scanning electron micrographs of honeycomb film cast under humidity of 80% R.H and a flow of 4 litres per minute. **(A) (B)** and **(C)** display the high order of the films produced over appreciable areas, **(D)** displays the morphology of the film underneath the top surface, **(E)** relationship between the average pore diameters and the number of PMMA arms of the star polymer, and **(F)** relationship between the average pore diameters and the molecular weight of the star polymer. Series A has PMMA arms with $M_n = 1.0 \times 10^4$ g mol^{-1} and Series B PMMA with $M_n = 2.0 \times 10^4$ g mol^{-1}.

Another significant report has been the preparation and control of porous films utilizing star functionality. Simply by changing the stars end group, dramatically different porous morphologies can be produced. This was achieved in a very controlled manner utilizing well defined dendrons based on 2,2-bis(methoxy)propionic acid (bis-MPA) as the stars end group. Three series of star polymers are prepared varying both the end group functionality and the size of the dendron. Initially, dendrons (generation 1 to generation 4) capable of initiating polymerization by ATRP were prepared.[6] Star polymers were then prepared as described in Scheme 1. Deprotection of the periphery groups creates hydroxyl functional star polymers, and these hydroxyl groups were then reacted with pentadecafluorooctanoyl chloride, to yield a third series of functional star polymers. These star polymers have surface groups with vastly different hydrophobicities. By utilizing these star polymers to form honeycomb films by the BF technique, a brand new method of control of the porous morphology is obtained (Figure 3).[7] The star polymers with amphiphilic character prepared interconnected porous morphologies with multiple layers of pores (Figure 3c). The star polymers with pentadecafluorooctanoyl end groups

4

showed highly ordered monolayers of pores with extremely thin walls – this is a new porous morphology which has never been reported (Figure 3c). This work has developed a new way to control the final porous morphology utilizing star polymer functionality.
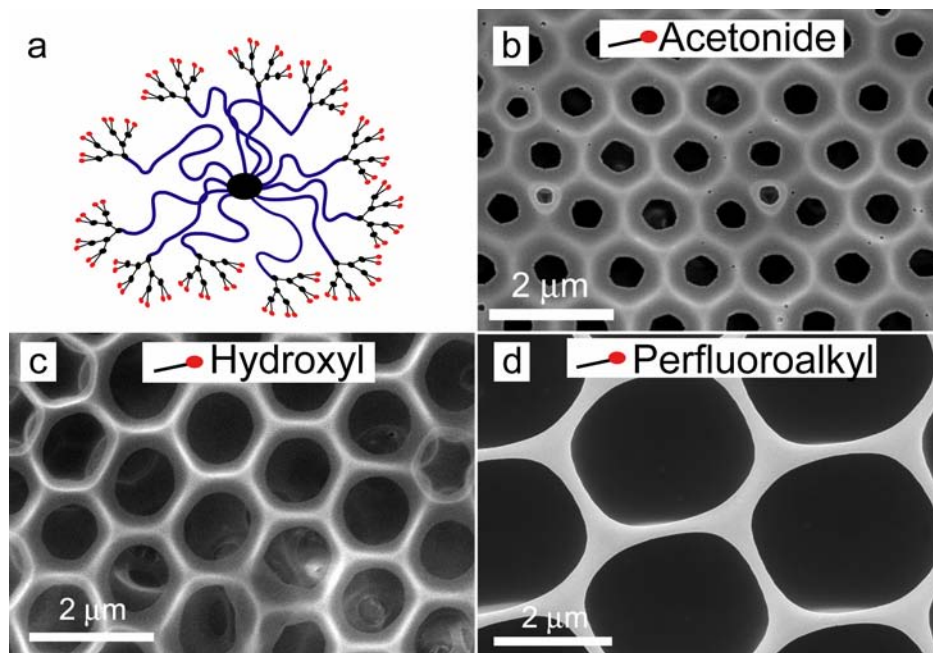

Figure 3. **(a)** idealized version of dendron functional star polymer; **(b)** scanning electron micrograph of honeycomb film formed from acetonide functional star polymer; **(c)** scanning electron micrograph of honeycomb film formed from hydroxyl functional star polymer; **(d)** scanning electron micrograph of honeycomb film formed from perfluoroalkyl functional star polymer.

Coating non-planar substrates

The patterning of polymeric thin films on flat substrates is a widely used and critically important technique in many industrial processes.[8] However, the conformal formation of highly ordered patterned films on non-planar substrates is significantly less developed even though these systems may pave the way for a new class of materials and microstructures. The facile preparation of porous materials on non-planar substrates, however, is not a trivial exercise.[9] Usually, the strategy involves the formation of a porous material and its transfer onto a curved substrate. Recently, we reported the first example of the preparation of porous honeycomb films that could contour to the surface of non-planar TEM grids.[10,11] Star polymers based on poly(dimethyl siloxane) (PDMS)

are used as a precursor for honeycomb materials made via the BF technique and TEM grids are used as the non-planar substrate (Figures 4a, 4f, and 4i). I described the successful formation of regular porous materials on these ordered non-flat substrates (Figures 4b, 4d, 4g, and 4j), these materials were used as soft lithography masters to produce a variety of exotic structures (Figures 2c, 4e and 4 k). This work greatly increases the versatility of the BF process.
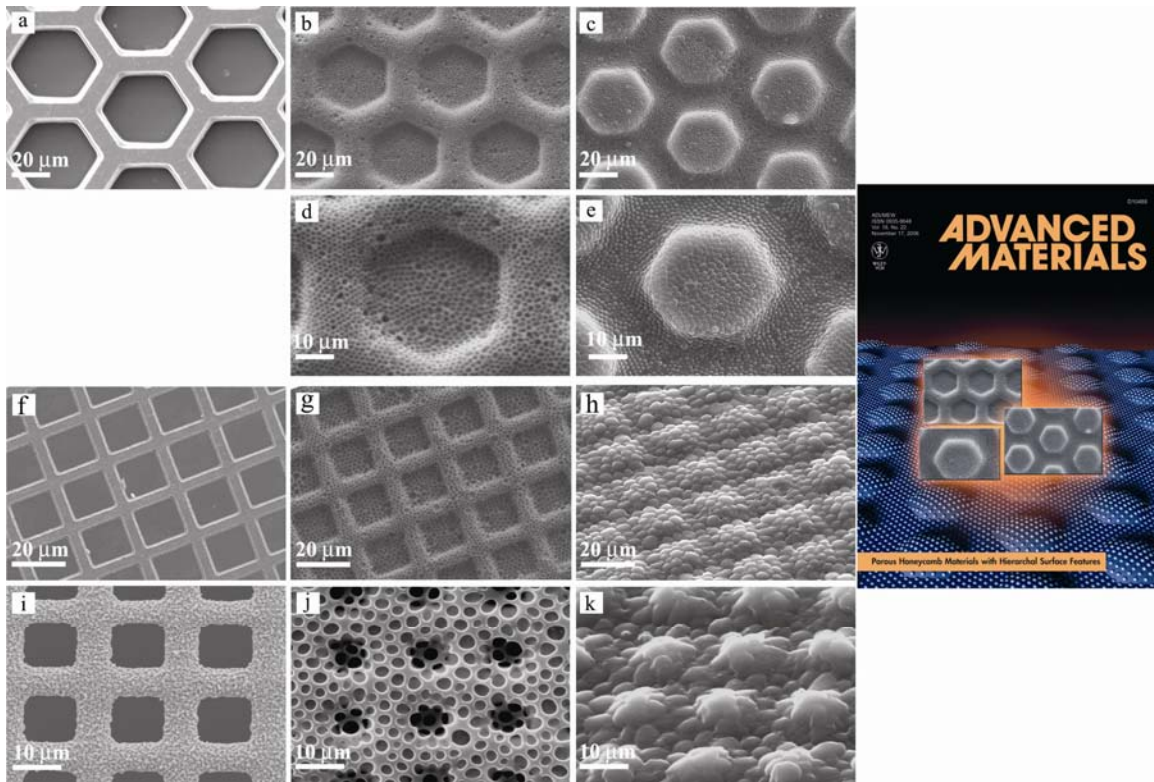

Figure 4. Scanning electron micrographs show the morphology of **(a)** hexagonal TEM grid with 6000 mesh; **(b)** honeycomb material formed on the surface of 600 mesh Hexagonal TEM grid; **(c)** negative image of honeycomb materials made by replica molding using *(b)* as a master; **(d)** higher magnification of *(b)*; **(e)** higher magnification of *(c)*; **(f)** square TEM grid with 1000 mesh; **(g)** honeycomb material formed on surface of 1000 mesh square TEM grid; **(h)** negative image of honeycomb materials made by replica molding using *(g)* as a master; **(i)** square TEM grid with 2000 mesh; **(j)** honeycomb material on surface of 2000 mesh square TEM grid; and **(k)** negative image of honeycomb materials made by replica molding using *(j)* as a master. Work featured on the cover of Advanced Materials, right-hand-side.

Coating particulate surfaces

I have developed a simple and general method for coating particle surfaces with honeycomb structure:[11,12] to the best of our knowledge, this is the first example of honeycomb films on particle surfaces, regardless of particle shape or surface chemistry (Figures 5a to 5e). It is envisaged that this technology could create functional porous chromatography particles, which could be applied in analytical chemistry.[13] Various water soluble particles (including salts) were introduced into the system to investigate the effect of removing the template after the honeycomb film is formed. Figure 5f shows the resultant structures after dissolving sugar crystals; a remarkable hollow microporous structure or "porous pockets" remain.
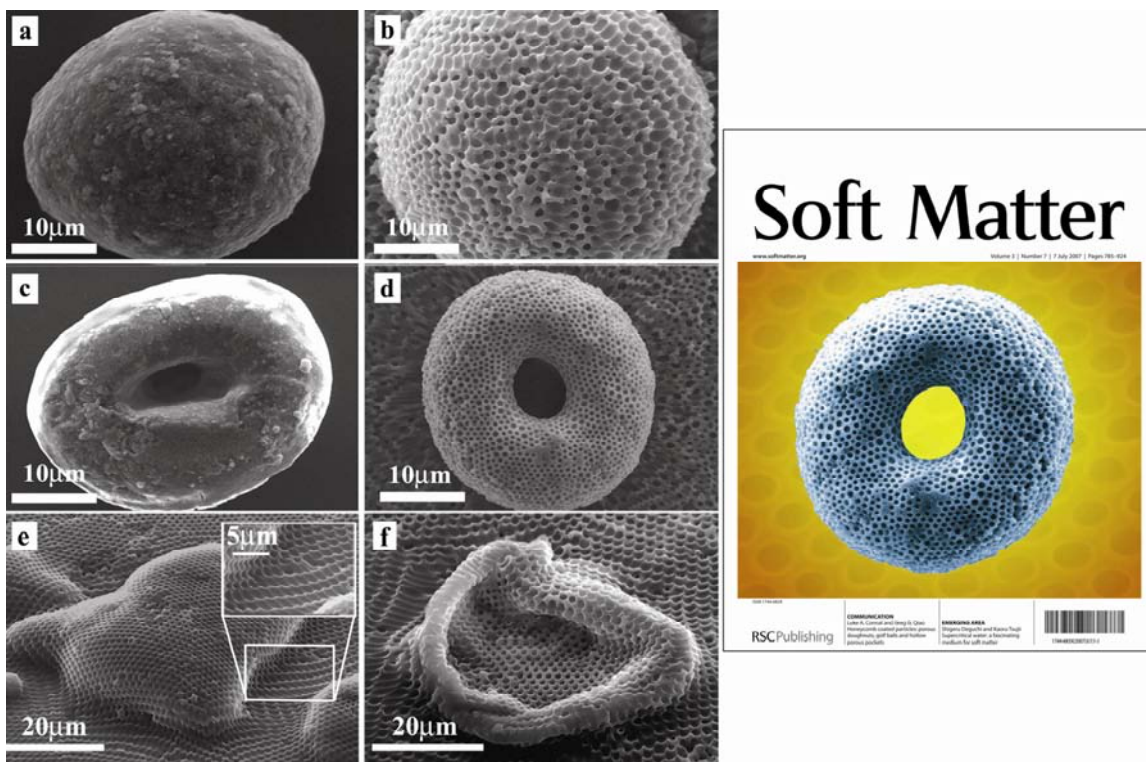

Figure 5. **a** and **b**: Scanning electron micrographs of a spherical kaolin particle on a glass surface (a) before and (b) after coating with PDMS star film with honeycomb morphology. **c** and **d**: Micrographs of a "doughnut" shaped kaolin particle on a glass surface (c) before and (d) after coated with PDMS star film. **e** and **f** micrographs of sugar crystal, coated with star PDMS honeycomb film, (c) before and (d) after dissolution of sugar crystal. Work featured on the cover of Soft Matter, right-hand-side.

Multifaceted porous materials

For these honeycomb materials to realize their potential in many applications, a higher degree of structural integrity is important; crosslinking materials can greatly increase their applicability in a range of areas. In a recent study, multifaceted porous materials were prepared through careful design of star polymer functionality and properties.[14] Functionalized poly(methyl acrylate) based CCS polymers were prepared having a multitude of hydroxyl groups at the chain ends. Modification of these chain ends with 9-anthracene carbonyl chloride introduced the ability to reversibly photo-crosslink these systems. The properties of the low T_g CCS polymer allow for the formation of porous films on non-planar substrates without cracking and photo-crosslinking allows the creation of stabilized honeycomb films while also permitting a secondary level of patterning on the film, using photolithographic techniques. These multifaceted porous polymer films represent a new generation of well-defined, 3D microstructures. Figure 6 describes the photo-lithography of honeycomb films. Figure 7a shows a honeycomb film patterned as described in Figure 6b, whereby the film was crosslinked in the presence of a photomask. The darker areas of the image are regions that are crosslinked as upon dimerization of the anthracene moiety the fluorescence decreases. Figure 7b shows the reversibility of this process; this film was crosslinked with a mask (described in Figure 6b), the mask was then removed and further irradiated (under crosslinking conditions, described in Figure 6c), effectively erasing the pattern. Then the film was uncrosslinked with a mask (described in Figure 6d), rewriting the reverse pattern into the film.
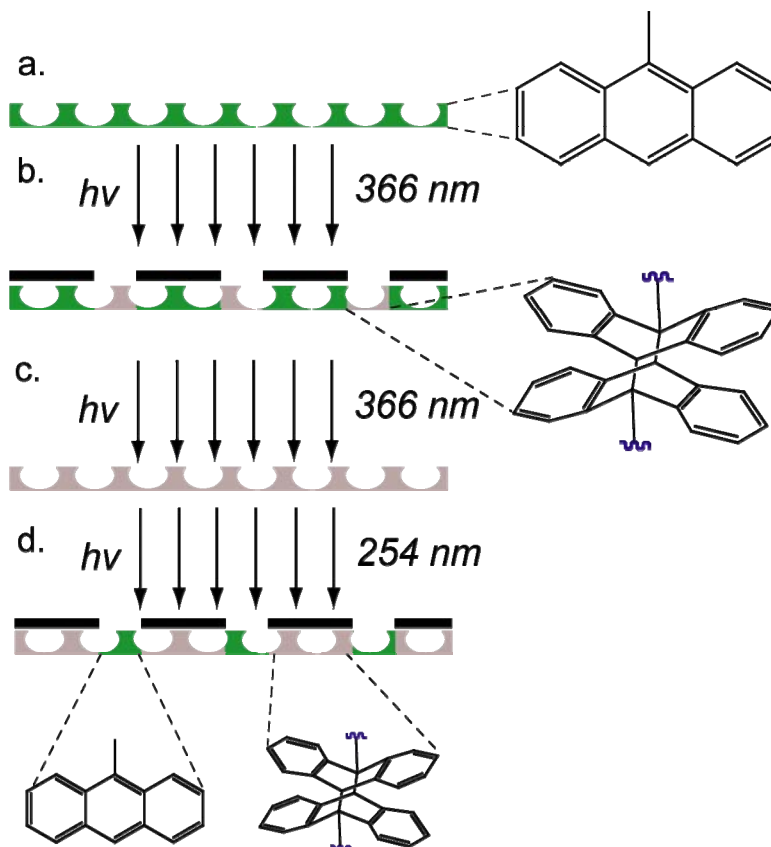
Figure 6 - Schematic representation of photo-lithographic transfer using a TEM grid as a mask. (a) As cast honeycomb film with fluorescent anthracene; (b) photo-lithographic patterning of honeycomb films using a mask, crosslinking the exposed areas with 366nm light; (c) removal of the mask and further irradiation with 366nm light erases the pattern; and (d) The TEM grid was then used again to rewrite into the film, this time with the 254nm light therefore creating the inverse pattern.

The methods described above can also be used to create honeycomb patterned films in discrete areas.[14] This was accomplished by washing the film away with tetrahydrofuran. Figure 8 shows the electron micrographs of a honeycomb film photo-patterned and then washed, removing certain areas of the film.
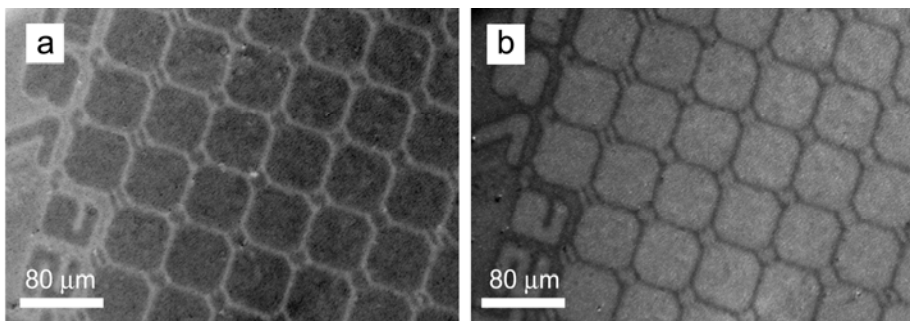
Figure 7 – Fluorescent microscope images of photo-induced patterning of honeycomb films cast from anthracene functional poly(methyl acrylate) star polymer, using a TEM grid as a photo-mask. (a) Initial irradiation with 366 nm light; (b) this surface has been irradiated further without the TEM grid at 366 nm light, erasing the pattern shown in (a), the grid was then placed back on the film and then irradiated with 254 nm light.
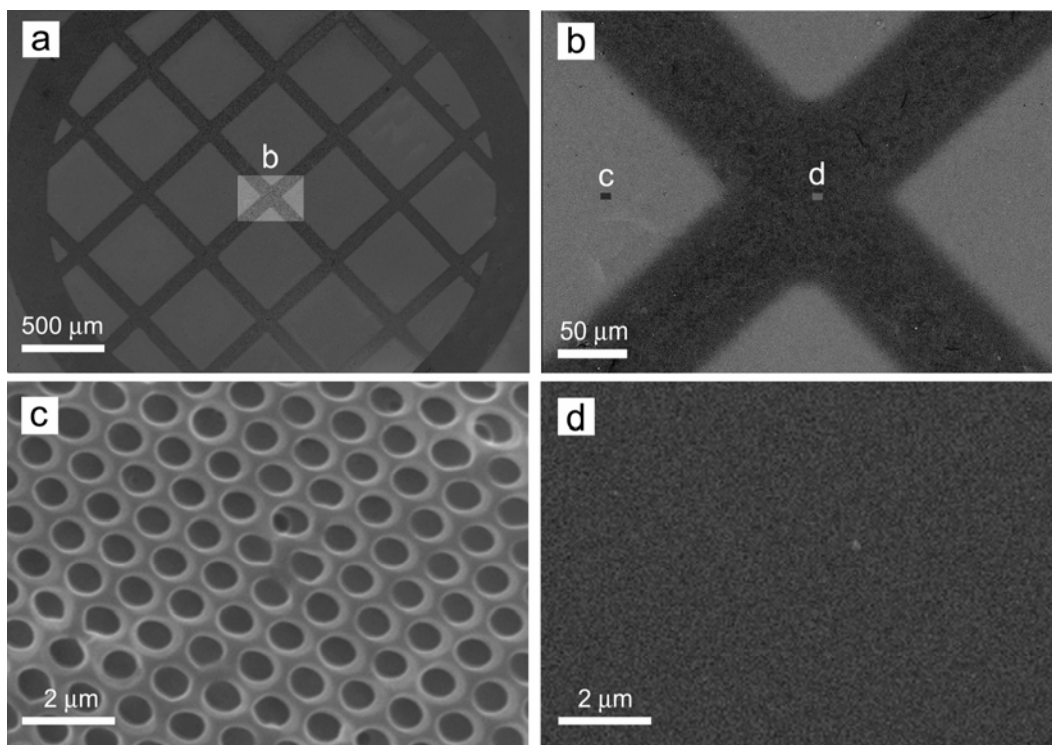

Figure 8 - Scanning electron micrographs of photo-patterned honeycomb materials. Anthracene functional PMA star polymer was cast under BF conditions and a TEM grid was then placed onto the surface and the film was placed under 366 nm UV light to crosslink the exposed areas. This film was then washed with THF to remove the uncross-linked material, leaving the TEM-grid induced pattern; **(a)** low magnification displaying the pattern from TEM grids; **(b)** medium magnification of area highlighted in (a); **(c)** high magnification of area highlighted in (b) showing where honeycomb structure remains; **(d)** high magnification of area highlighted in (b) highlighting the area where the honeycomb structure has been washed away.

Conclusions

The methods and results obtained from my doctoral studies have greatly increased the applicability of honeycomb materials; from control of porous structures to crosslinkable, three dimensionally conformable microstructured films.

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