

Honeycomb Films from Perfluoropolyether-Based Star and Micelle Architectures

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A perfluoropolyether-*b*-poly(*t*-butyl acrylate) (PFPE-*b*-PtBA) block copolymer macroinitiator was used to prepare both core cross-linked star (CCS) polymers and micelles, whereby the outer shell and core, respectively, are comprised of fluorinated segments. The star polymer complete with PFPE outer shell was synthesised via atom transfer radical polymerisation (ATRP) and the arm-first approach, through cross-linking of the PFPE-*b*-PtBA macroinitiator with ethylene glycol diacrylate (EGDA). Alternatively, the PFPE-*b*-PtBA block copolymer could be self-assembled in benzene to form micelles with a PtBA shell and PFPE core. Both the micelle and CCS polymer were subsequently fabricated into non-cracking honeycomb (HC) patterned films on both planar and non-planar surfaces via the ‘Breath Figure’ (BF) technique using a static casting system.

Manuscript received: 21 May 2012.

Manuscript accepted: 22 June 2012.

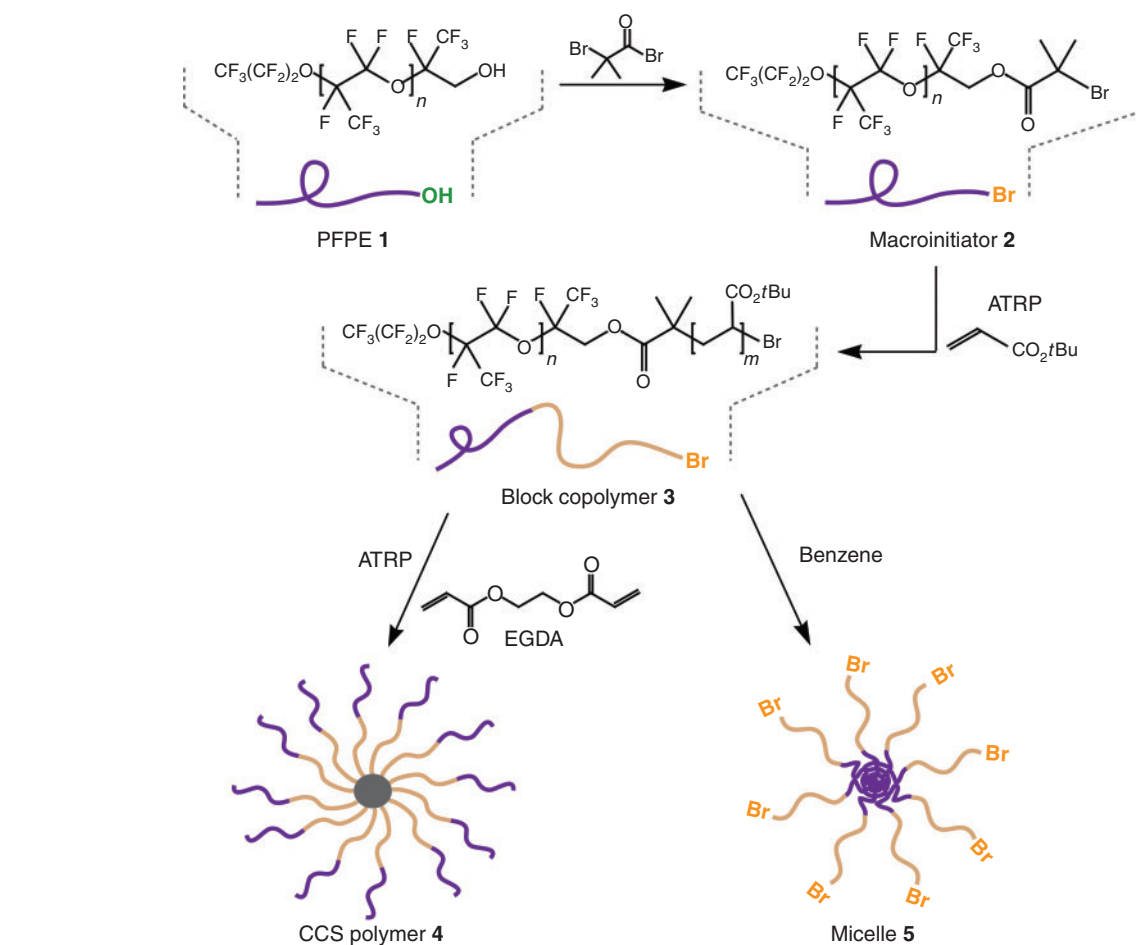
Published online: 17 July 2012.

The ‘Breath Figure’ (BF) technique is well known as a robust and highly efficient approach for the preparation of highly ordered porous films on planar and non-planar substrates.^[1–5] It was first introduced by François and co-workers, wherein highly ordered HC films were achieved by casting solutions of star-like polystyrene under a humid environment.^[6] Recently, the development, progress and applications of HC films were reviewed by Hernández-Guerrero and Stenzel.^[7] Highly ordered HC patterned films are of great interest due to their wide range of potential specialised and high value applications such as optical and electronic devices,^[8] energy storage,^[9] catalyst supports,^[10] templates,^[11] cell culture scaffolds,^[12] and fluorinated superhydrophobic surfaces.^[13] Perfluorinated polymers such as PFPEs are of great interest to biomedical engineering and polymer therapeutics as a result of their unique properties,^[14,15] including high thermal stability, chemical resistance in highly aggressive media, low flammability, and negligible toxicity.^[16,17] Although research has been undertaken to develop PFPE porous films for biomedical applications, they lack an ordered HC structure, and the fabrication processes are complex and non-uniform.^[18] Herein, we describe the synthesis of CCS polymers^[19] and micelles containing PFPE segments localised to their outer shell and core, respectively, and the preparation of the corresponding PFPE-based HC patterned films.

Due to the poor solubility/processability and low melting point of PFPEs, it is not possible to form HC films from PFPEs alone. Therefore, ATRP was employed to prepare a PFPE-based copolymer (Scheme 1). Initially, a monohydroxy terminated PFPE (poly(perfluoropropylene oxide)), was functionalised

with an alkyl bromide suitable for ATRP through reaction with bromoisobutryl bromide. As shown in Scheme 1, the monohydroxy PFPE **1** was reacted with 2-bromoisobutryl bromide to form macroinitiator **2** containing a terminal bromine moiety (PFPE-Br). Macroinitiator **2** was then used to polymerise *t*-butyl acrylate (*t*BA) via ATRP to form the PFPE-*b*-PtBA block copolymer **3**. The formation of a star restricts the PFPE segment to the outer shell (covalently), whereas this may not be possible using self-assembly alone. Hence, the diblock copolymer **3** was reacted with cross-linker EGDA via ATRP to afford CCS polymer **4** with a hydrophobic PFPE outer shell and alkyl acrylate inner shell and core. Alternatively, an inverse structure with a PFPE core and a PtBA shell was prepared by dissolving the copolymer **3** in benzene, which resulted in the formation of micelle **5** through self-assembly.

The successful synthesis of polymers **1–4** was confirmed by nuclear magnetic resonance (NMR) spectroscopy, matrix assisted laser desorption ionisation time-of-flight (MALDI ToF) mass spectrometry and gel permeation chromatography (GPC). The successful conversion of the monohydroxy PFPE **1** (Figure S1 in the Supplementary Material) to macroinitiator **2** was confirmed by MALDI ToF mass spectrometry (Fig. 1a), which revealed a shift of the oligomer series to higher mass and peak mass values corresponded to the expected structure complete with characteristic bromine isotope splitting patterns. The number-average molecular weight (M_n) and polydispersity index (PDI) of macroinitiator **2** was determined by MALDI ToF mass spectrometry to be 1.8 kDa and 1.08, respectively. Chain extension of the macroinitiator **2** with *t*BA afforded the



Scheme 1. Synthetic outline showing the conversion of the monohydroxy PFPE **1** to the PFPE macroinitiator **2**, followed by ATRP with *t*-butyl acrylate to afford the PFPE-*b*-PtBA block copolymer **3**. Subsequent reaction of the copolymer **3** with cross-linker via ATRP or self-assembly in selective solvent affords the core cross-linked star polymer **4** and micelle **5**, respectively.

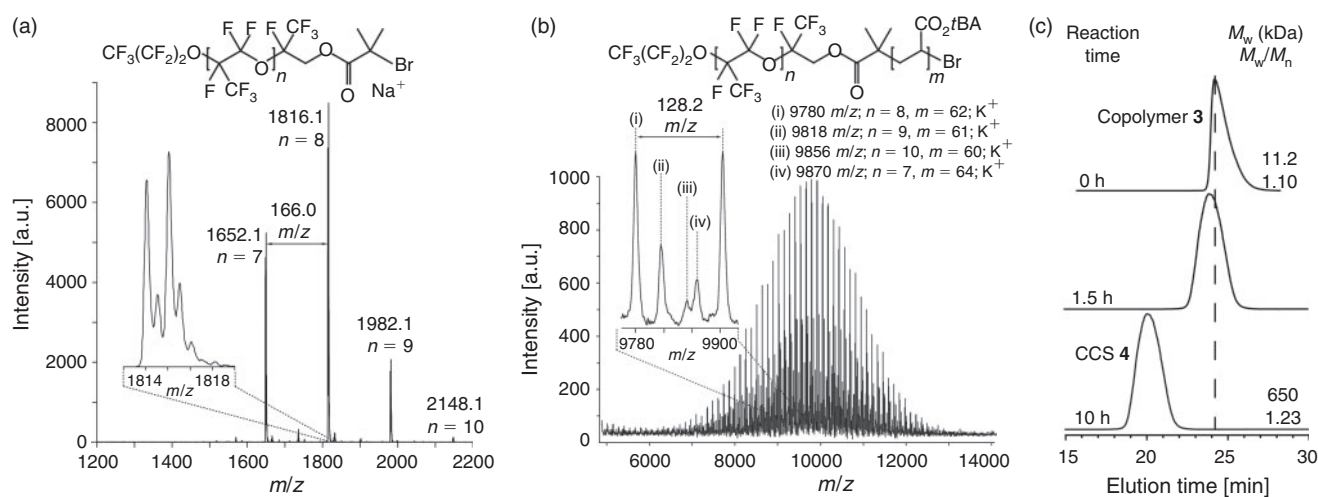


Fig. 1. MALDI ToF mass spectra of (a) PFPE macroinitiator **2** and (b) PFPE-*b*-PtBA block copolymer **3** recorded in linear/positive mode using NaCl/perfluorobenzoic acid and potassium trifluoroacetate (KTFA)/*trans*-2-[3-(4-*tert*-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the cationisation agent/matrix, respectively. (c) GPC differential refractive index (DRI) chromatograms of block copolymer **3** and formation of CCS polymer **4** after 1.5 and 10 h.

PFPE-*b*-PtBA block copolymer **3**, with a M_n of 10.2 kDa as determined by GPC (Fig. 1c). In addition, the narrow PDI (1.10) obtained from GPC indicates good control over the polymerisation and a well defined copolymer structure. MALDI ToF mass

spectrometry of the copolymer **3** revealed a symmetrical mass distribution with four series of peaks (corresponding to $n=7-10$) separated by the mass of the PFPE and *t*BA repeat units (Fig. 1b). The mass values were found to correlate well

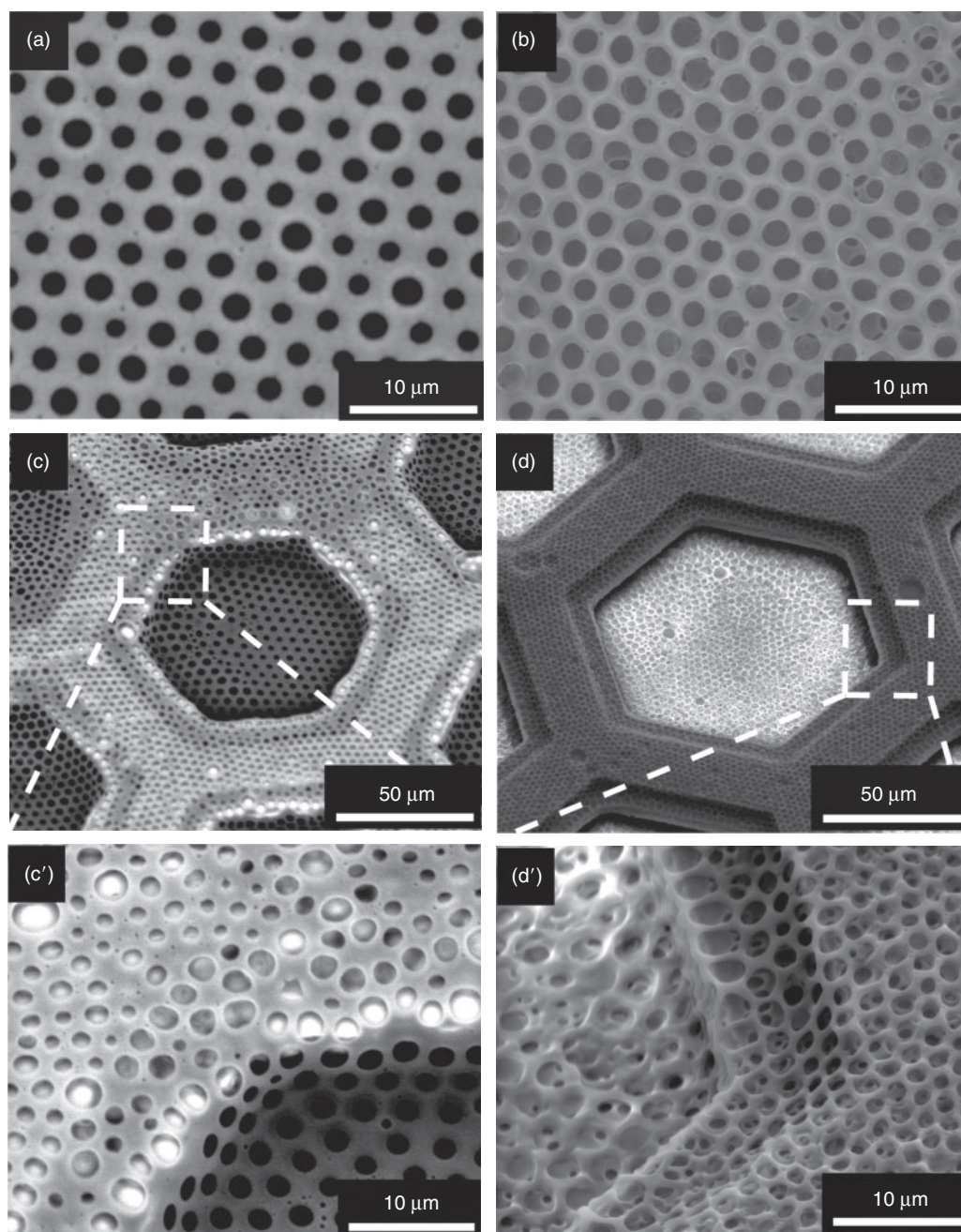


Fig. 2. Scanning electron microscopy images of honeycomb films formed on both planar and non-planar substrates. Planar surface: (a) star polymer **4** and (b) micelle **5**. Non-planar surface: (c and c') star polymer **4** and (d and d') micelle **5**.

with the desired copolymer structure complete with bromine end groups and provided a M_n of 9.8 kDa, which is very similar to the value determined by GPC. Subsequently, the block copolymer **3** was cross-linked together via ATRP to afford a CCS polymer using EGDA. The reaction was followed by GPC, which revealed a smooth shift of the copolymer peak to lower retention time after 1.5 h, indicating chain extension with the cross-linker. Interestingly, after 10 h a complete shift from the original block copolymer **3** peak (at 24 min) was observed, confirming the formation of higher molecular weight species, which was assigned to the star polymer **4** ($M_n = 650$ kDa, PDI = 1.23). The average number of arms (f) of each star was determined to be 49.^[19] To achieve quantitative conversion of the macro-initiator-to-star required optimisation of the reaction conditions,

with a solvent ratio of 10 : 1 toluene : trifluorotoluene proving to be optimal. When only toluene was used gelation occurred, possibly as a result of the self-assembly of the copolymer **3** into micelles whereby the PFPE blocks make up the core, the PBA blocks the shell, and the bromine groups are located at the periphery. Therefore, the pre-organisation of the copolymers would hinder star formation and favour gelation since the cross-linker would polymerise outwards from the active bromine terminals located on the periphery of the micelle. The high conversion of block copolymer **3** to CCS polymer **4** indicates excellent control over the polymerisation under these conditions and the highly 'living' nature of the copolymer **3**.

Self-assembly of copolymer **3** to afford micelle **5**, which has the inverse structure of CCS polymer **4**, was conducted in

benzene. Benzene was chosen due to the good solubility of PtBA in this solvent and the poor solubility of PFPE. Thus, the copolymer would be expected to aggregate and self-assemble in such a way that the PFPE block would be shielded from the solvent by the PtBA block. Furthermore, benzene is a suitable solvent for HC film formation. Self-assembly of the block copolymer **3** in benzene (15 mg mL^{-1}) was followed by dynamic light scattering (DLS) analysis, which revealed the successful formation of micelles having an average size of $\sim 400 \text{ nm}$ and polydispersities of between 0.2 and 0.3 (Figure S2 in the Supplementary Material).

In order to assess the difference in the surface hydrophobicity of films prepared from the CCS polymer **4** and micelle **5**, planar non-porous films and porous HC films were prepared. Non-porous films were prepared from solutions of CCS polymer **4** and micelle **5** in benzene (15 mg mL^{-1}) cast onto flat glass coverslips and left to dry at room temperature ($\sim 20\%$ relative humidity (RH)). In comparison, the casting of planar HC films was conducted via a static casting process (without air flow), whereby the polymer solutions were cast onto flat glass coverslips under a humid environment ($\sim 70\%$ RH). Measurement of the contact angle of the planar non-porous films and porous HC films formed from both polymers (Figure S3 in the Supplementary Material) revealed that films prepared from micelle **5** had a lower contact angle than films prepared from star polymer **4**. For example, the non-porous film formed from star polymer **4** had a contact angle of 101.3° (Figure S3b in the Supplementary Material) compared with 93.0° for the film formed from micelle **5** (Figure S3a in the Supplementary Material). The hydrophobicity difference of these two films results from the structure of star polymer **4** and micelle **5** and the resulting location of the perfluorinated segments within the film. For example, the hydrophobic perfluorinated outer shell of star polymer **4** would be expected to reside close to the external surfaces of the film, whereas the core isolated perfluorinated blocks of micelle **5** would be expected to reside in the bulk of the film. In comparison, the contact angles for the porous HC films were enhanced to 108.7° and 125.6° for the micelle **5** and star polymer **4** films, respectively (Figure S3c and S3d in the Supplementary Material), and is a direct result of the HC pattern increasing the surface roughness, and therefore the hydrophobicity of the film, which is consistent with the results of Yabu et al.^[20] Moreover, the surface hydrophobicity of HC film prepared from star **4** (18 wt-% PFPE) is similar to that of a microporous film made from pure PFPE.^[21]

Scanning electron microscopy (SEM) imaging of the porous HC films revealed that both star polymer **4** and micelle **5** (Fig. 2a and b, respectively) form very uniform HC patterns. The average pore size of the HC films prepared from star **4** and micelle **5** was determined to be 4.10 and $3.33 \mu\text{m}$, whereas the average surface pore opening size was ~ 2.0 and $1.8 \mu\text{m}$, respectively. Non-planar HC films were prepared by casting the polymer solutions onto TEM grids placed on glass coverslips using the same casting conditions used for planar HC films. SEM imaging of the resulting films revealed that both the star polymer and micelle were capable of replicating the surface structure of the TEM grids (Fig. 2c and 2d). Moreover, the films retained an ordered porous structure at the 'stair-like' sharp edges of the TEM grid without cracking (Fig. 2c' and 2d').

In conclusion, we have successfully prepared a well defined perfluoropolyether (PFPE)-based block copolymer with good solubility and processability characteristics. The copolymer was subsequently cross-linked via ATRP to afford a star polymer

with fluorinated outer shell, or self-assembled in benzene to afford a micelle with fluorinated core. Interestingly, complete conversion of the copolymer to star polymer was observed indicating the highly living nature of the copolymer. Both the star polymer and micelle readily formed honeycomb patterned films on planar surfaces and displayed different surface hydrophobicities as a result of the location of the fluorinated block. Non-planar honeycomb films were also fabricated on TEM grids. The non-planar PFPE honeycomb films were found to contour to the TEM grid surface structure while still maintaining an ordered porous pattern. Therefore, for the first time we have demonstrated that PFPE-based polymers can form honeycomb structured films on both planar and non-planar surfaces. This study demonstrates a robust way for fabricating highly ordered PFPE-based porous films, which have potential applications as cell culture substrates and tissue engineering scaffolds.

Experimental

Planar and Non-Planar HC Film Casting

HC films were prepared by first stabilising the conditions of the casting environment to $\sim 30^\circ\text{C}$ and $70 \pm 5\%$ RH. The star polymer and diblock copolymer were dissolved in benzene (15 mg mL^{-1}). $20 \mu\text{L}$ of the solution was then dropped carefully onto a circular glass coverslip (planar surface) or a TEM grid placed on a glass coverslip (non-planar surface) and the solvent and water left to evaporate.

Supplementary Material

Full synthetic details and characterisation of the starting materials, precursors, star polymer, and micelle are available on the Journal's website.

Acknowledgements

The authors acknowledge CSIRO and The University of Melbourne for providing scholarships to ZZ. The authors also acknowledge Prof. Qing for the donation of the monohydroxy PFPE and the Electron Microscopy Unit at the Bio21 institute (The University of Melbourne) for assistance with SEM.

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