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# Influence of Polymer Elasticity on the Formation of Non-Cracking Honeycomb Films

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The Breath Figure (BF) technique is a well established, robust and highly efficient approach for the preparation of highly ordered porous films.[1] It was first introduced by François and co-workers, whereby water droplets were utilised as templates for the self-assembly of polymers to form highly ordered honeycomb (HC) films.[2] HC structured films have also been prepared using lithographic and other non-lithographic patterning methods, although these methods are expensive and/or complex.[3,4] Numerous polymer architectures have been employed with the BF technique to prepare ordered macroporous and microporous HC structures on flat surfaces.[5–11] Highly ordered HC patterned films are of great interest due to their wide range of potential specialised and high value applications including biosensors,[12] membranes,[13] scaffolds for tissue engineering,[10,14] microreactors,[15] photonic band gap devices,[16] and optoelectronic devices.[17] Recently, Fujifilm has developed a technique to produce large areas of HC films with minimal defects on flat substrates.[18] However, the applicability of this technique to non-planar surfaces is unknown. Cracking or fracture of the film remains a major issue during the formation of non-planar HC films, resulting in poor reproducibility. Methodologies that enable HC films to be reproducibly prepared over large imperfect surfaces (e.g., non-planar surfaces) will facilitate commercial uptake of this micro-fabrication technique to a wide variety of surfaces. Therefore, the development of strategies for the fabrication of regularly patterned films on rough surfaces and the ability to select precursors from a wide range of polymers with varied composition will significantly expand the scope of applications where HC films can be applied. In 2006 we reported the first example of HC formation on non-planar surfaces using star polymers with low glass transition temperatures ($T_g$'s).[7,8,19] Highly conformal non-planar HC films were successfully prepared without cracking on the surface of transmission electronic microscopy (TEM) grids as well as other non-planar surfaces.[8] During an investigation of a series of star polymers made from poly(dimethylsiloxane) (polyDMS), poly(methyl acrylate) (polyMA), poly(*tert*-butyl acrylate) (poly*t*BA) and poly(methyl methacrylate) (polyMMA), it was observed that the $T_g$ of these polymers played an important role in the process of non-planar porous film formation. It was found that all these polymers could form regular HC structures on planar surfaces without the occurrence of cracking. However, the polymers with a $T_g > 48$ °C formed HC films on non-planar surfaces with cracks while polymers with a $T_g \leq 48$ °C formed HC films that contoured to the TEM grid surface without cracking. Similar phenomena were also later reported by Tian and co-workers.[20] Until now it has remained unclear if $T_g$ is the only parameter that determines the repetitive formation of conformal HC patterned films on non-planar surfaces for star polymer systems.

In this communication, we report that there are parameters other than $T_g$ that have a significant influence on the formation of non-cracking HC films when a broad range of polymers are used. More specifically, a polymer's elasticity, represented as the Young's modulus, can be used to better predict if a well-defined, conformal and non-cracking HC film will be formed on non-planar surfaces. In this study the Young's modulus ($E$) is used to define the tensile elasticity of the polymeric films and we demonstrate that tuning the $E$ of polymers can regulate the formation of non-cracking HC films on non-planar surfaces; this observation applies to seven of the polymers investigated in this study, including polymers with various $T_g$'s. With appropriate design, a polymer with a high $T_g$ and suitable $E$ could potentially be employed to form non-cracking HC films on non-planar substrates, which may ultimately lead to more and new industrial applications of this technology.

Star polymers were chosen as candidates for the HC film formation based upon previous studies.[7,9] A series of $\beta$-cyclodextrin ($\beta$-CD)-based star polymers with varying $T_g$ and $E$ were designed and synthesised via atom transfer radical polymerisation (ATRP) and the 'core-first' approach (**Scheme 1**).[21] Subsequently, the formation of HC films on planar and non-planar surfaces was investigated using these star polymers and an improved static casting method employing a warm (30 °C) humid environment.[11]

Initially, a bromoester functionalised $\beta$-CD derivative with 21 initiating sites was prepared from the reaction of $\beta$-CD with 2-bromopropanoyl bromide (Scheme 1 and Figure S1).[22] Using this initiator, one-pot ATRP reactions were performed with a range of monomers or combinations of monomers to form star polymers with varying $T_g$ and $E$. These monomers include methyl methacrylate (MMA), methyl acrylate (MA), *tert*-butyl

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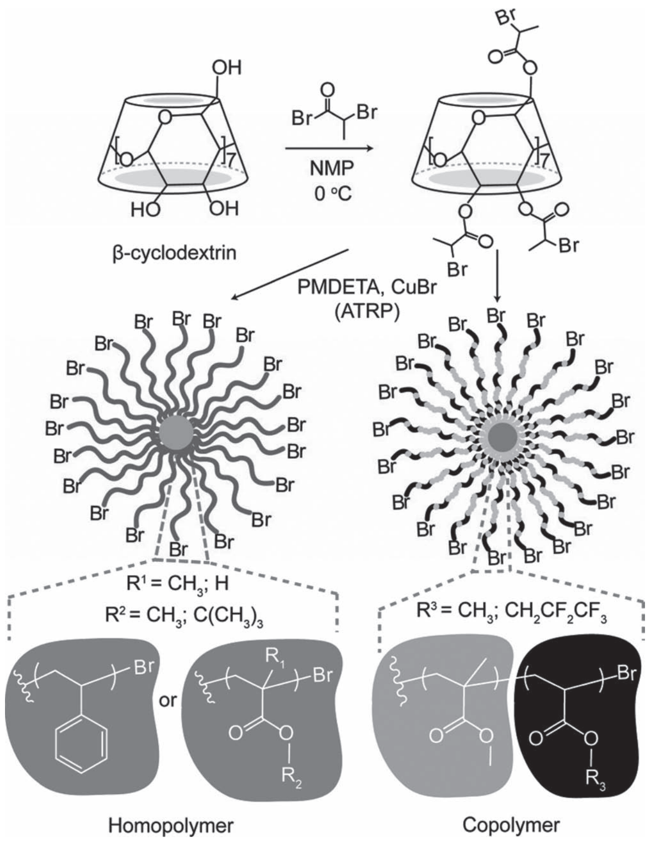

**Scheme 1.** Synthesis of star polymers via ATRP and the core-first approach using an initiator functionalised *β*-cyclodextrin derivative.

acrylate (*t*BA), styrene (St) and *1H,1H*-pentafluoropropyl acrylate (PFPA) to afford polyMMA, polyMA, poly*t*BA, polySt, poly(MMA-*co*-MA), and poly(PFPA-*co*-MMA) star polymers, respectively. These star polymers can be divided into three series: (1) copolymers of MMA and PFPA (**C1a-d**); (2) copolymers of MMA and MA (**C2a-f**); and (3) various homopolymers (**H1-4**) (**Table 1**). Given the known reactivity ratios of MMA relative to PFPA or MA, the copolymer arms of the star polymers prepared from MMA and PFPA or MMA and MA are likely to have gradient structures (ESI). The weight-average molecular weight ($M_w$) and polydispersity index (PDI) values (Table 1) of the star polymers were determined by gel permeation chromatography (GPC) equipped with a multiangle laser light scattering detector (MALLS). In all cases the star polymers displayed narrow PDI values (≤1.22), which is indicative of good control over the polymerisation process. The $T_g$ values of the polymers were measured using differential scanning calorimetry (DSC) and ranged from 2 to 100 °C. It has previously been reported that atomic force microscopy (AFM) can be used to determine Young's modulus (*E*) of both thin films and bulk materials.[23] Accordingly, the *E* values of thin non-porous polymer films (ca. 1 μm) prepared from the star polymers on glass cover slips were measured via AFM (Table 1) and found to range from 0.018 to 5.92 GPa. By careful design, it was possible to prepare polymers with similar $T_g$ values but different *E* values. For example, copolymers **C1b** and **C2b** both have $T_g$ values of *ca*. 75 °C, however, their *E* values are 4.63 and 5.24 GPa, respectively. Interestingly, the *E* was found to decrease as the $T_g$ decreased regardless of the type of star polymers investigated (Table 1). Furthermore, for copolymer series 1 and 2 an increase in the PFPA (**C1a** to **C1-d**) or MA (**C2a** to **C2f**) component resulted in decreases in both the $T_g$ and *E*, demonstrating that the fluorine or MA content can be used to tailor specific $T_g$ and *E* values.

Planar HC films were prepared via a static casting process, whereby solutions of star polymers in chloroform (5 mg mL$^{-1}$) were cast onto flat glass cover slips under a humid environment (*ca*. 70% relative humidity (RH)) without air flow. This

**Table 1.** Characterisation of star polymers.

| Series | Star polymer arm composition[a] | Polymer code[b] | $M_w$[c] [kDa] | PDI[c] | $T_g$[d] [°C] | $E$[e] [GPa] | Non-planar HC film |
|---|---|---|---|---|---|---|---|
| 1 | Poly(PFPA$_1$-*co*-MMA$_{27}$) | **C1a** | 66.5 | 1.07 | 94.5 | 5.07 | Non-cracking |
|  | Poly(PFPA$_3$-*co*-MMA$_{100}$) | **C1b** | 225.0 | 1.15 | 74.1 | 4.63 | Non-cracking |
|  | Poly(PFPA$_{17}$-*co*-MMA$_{35}$) | **C1c** | 153.9 | 1.22 | 53.5 | 4.25 | Non-cracking |
|  | Poly(PFPA$_8$-*co*-MMA$_6$) | **C1d** | 51.1 | 1.11 | 21.8 | 3.50 | Non-cracking |
| 2 | Poly(MMA$_{30}$-*co*-MA$_3$) | **C2a** | 72.3 | 1.09 | 83.5 | 5.25 | Cracking |
|  | Poly(MMA$_{16}$-*co*-MA$_2$) | **C2b** | 42.4 | 1.07 | 75.9 | 5.24 | Cracking |
|  | Poly(MMA$_{26}$-*co*-MA$_4$) | **C2c** | 65.6 | 1.07 | 71.1 | 5.23 | Cracking |
|  | Poly(MMA$_{22}$-*co*-MA$_4$) | **C2d** | 58.1 | 1.08 | 61.5 | 5.20 | Cracking |
|  | Poly(MMA$_{20}$-*co*-MA$_5$) | **C2e** | 54.8 | 1.07 | 57.5 | 5.15 | Cracking |
|  | Poly(MMA$_{28}$-*co*-MA$_8$) | **C2f** | 77.6 | 1.05 | 53.9 | 5.10 | Non-cracking |
| 3 | PolyMMA$_{46}$ | **H1** | 100.0 | 1.10 | 100.0 | 5.25 | Cracking |
|  | PolySt$_{27}$ | **H2** | 53.1 | 1.09 | 95.0 | 5.96 | Cracking |
|  | Poly*t*BA$_{13}$ | **H3** | 39.1 | 1.10 | 48.0 | 0.066 | Non-cracking |
|  | PolyMA$_{21}$ | **H4** | 50.2 | 1.08 | 2.0 | 0.018 | Non-cracking |

[a] Composition of copolymers determined via $^1$H NMR spectroscopic analysis; [b] C and H refer to copolymer and homopolymer, respectively; [c] Weight-average molecular weight of star polymers determined by GPC-MALLS and based upon the assumption of 100% mass recovery; [d] Glass transition temperature determined by DSC; [e] Young's modulus determined by AFM.

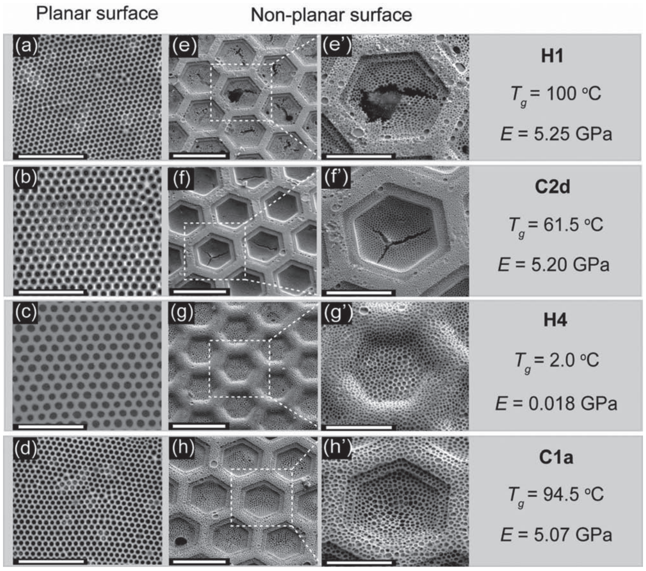

**Figure 1.** SEM images of polymer films with HC morphology prepared from star polymers **H1**, **C2d**, **H4**, and **C1a** on (a–d) planar and (e–h and e′–h′) non-planar substrates. Scale bars: (a–d) 10 µm, (e–h) 100 µm, (e′–h′) 50 µm.

approach potentially allows large areas to be uniformly coated since it eliminates complications associated with maintaining an even and constant air flow across the surface. The resulting films were analyzed by scanning electron microscopy (SEM). As expected, all the star polymers formed HC patterned films on flat glass surfaces and the thickness of the films was *ca*. 2 µm as determined by AFM scratch analysis; four SEM images are shown as representative examples (**Figure 1**a–d). Non-planar HC films were prepared by casting onto TEM grids placed on glass cover slips using the same method and casting conditions as used for planar HC films. SEM imaging of the films cast from solutions of star polymers **H1**, **C2d**, **H4** and **C1a** (Figure 1e–h and e'-h') on hexagonal TEM grids (300 mesh) revealed that all of the star polymers formed HC patterned films.

Previously, it was proposed that there was an upper $T_g$ limit of 48 °C for the formation of non-cracking HC films on non-planar surfaces.[5,8,19] However, interestingly, star polymer **C1a** (Figure 1h) with a $T_g$ of 94.5 °C, much higher than the proposed upper $T_g$ limit (48 °C), successfully formed a well-conformed film on the non-planar surface, which contoured well with the surface of the TEM grid and, importantly, displayed no cracking. In comparison, the non-planar films prepared from star polymers **H1** and **C2d** (Figure 1e and f, respectively) displayed significant cracking. Although **C1a**, **H1** and **C2d** all possess $T_g$'s above 48 °C, only **C1a** with a relatively low $E$ showed non-cracking. Not surprisingly star polymer **H4**, which has an even lower $E$ of 0.018 GPa readily forms HC structures without cracking (Figure 1g). Moreover, other star polymers with relatively low $E$ including **C1b**, **C1c** and **C2f** all formed non-cracking HC films on TEM grids even though their $T_g$ values are above 48 °C (Table 1 and Figure S2). These results strongly suggest that the $T_g$ alone is not an adequate factor for determining the formation of non-cracking films on non-planar surfaces. Rather, the elasticity of the polymers may be considered a more primary parameter in the formation of non-cracking HC films.

To eliminate casting solvent as a factor, non-planar HC formation was carried out using a range of solvents, including dichloromethane, carbon disulfide, benzene and toluene. SEM imaging of the resulting films (Figure S3) revealed that different solvents had little or no effect on the resulting HC films. Since the film thickness may have an influence on the cracking behaviour of the films, all the HC films in this study were prepared from solutions with identical polymer concentrations and were cast over the same area. Consequently, the films have similar thicknesses of ca. 2 µm as determined by AFM scratch analysis. Therefore, the comparison of film cracking behaviour is based on films with very similar thicknesses.

Based upon SEM images (Figure 1 and S2) of the HC films on non-planar substrates, all of the star polymers were simply labelled as cracking or non-cracking (Table 1), whereby any film with an observable crack anywhere in the image was deemed as cracking. In addition, a plot of $T_g$ versus $E$ for all polymers (**Figure 2**) indicates the presence of two regions corresponding to those polymers that formed cracking or non-cracking HC films on non-planar surfaces. In this case, a transition between cracking and non-cracking $E$ of ca. 5 GPa was observed. However, it should be noted that $E$ values measured by AFM are strongly influenced by the type of AFM tips used and the film thickness. For example, it has been shown that the measurement of the $E$ of polySt films varies depending on the AFM tip geometry and film thickness, with very thin films displaying significantly higher than average $E$ values.[23] Therefore, the $E$ values presented in this paper may not be absolute values, but rather describe a relative trend of polymeric elasticity properties. Polymers with relatively low $E$ are more likely to form non-cracking films on TEM grids. This demonstrates that the $E$ of a polymer plays a more important role in non-planar film casting than the polymers $T_g$. Thus, as described earlier, polymers with a relatively high $T_g$ (up to 94.5 °C) can still form highly conformal, non-cracking HC films on non-planar surfaces if they have a relatively low $E$. Star polymer synthesis involving the copolymerisation of PFPA or MA with a higher $T_g$ monomer (e.g., MMA) in a one-pot reaction affords star polymers possessing a high $T_g$ yet relatively low $E$ and can readily be employed to prepare non-planar HC films without cracking.

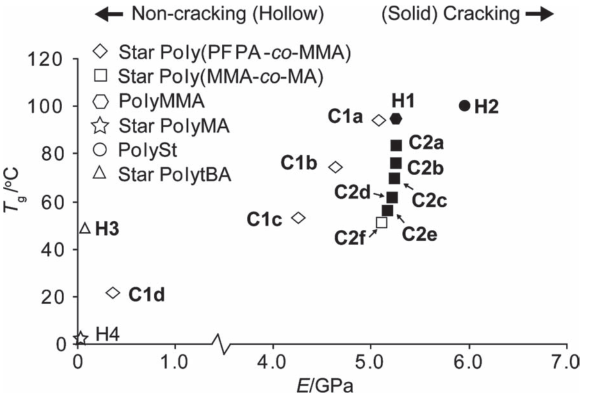

**Figure 2.** Glass transition ($T_g$) versus Young's modulus ($E$) for the star polymers.

In conclusion, we have successfully prepared a series of star polymers with different $T_g$ and $E$ values. The star polymer solutions were employed to prepare honeycomb (HC) patterned films on both planar and non-planar surfaces using a static casting method. For the first time, polymers with $T_g$ values as high as 94.5 °C were observed to form non-cracking HC structures on non-planar surfaces, which appear to result from the appropriate elasticity of the polymers, as dictated by their composition. This study demonstrates that the $E$ of a polymer is a more important factor, compared to $T_g$, in determining the occurrence of cracking during HC film formation on non-planar surfaces. This finding will have important implications for improving the repeatability of HC structure formation and enhance the suitability of HC films to more practical applications. Furthermore, this finding also provides access to the formation of HC films from a variety of different polymers not used before. It is envisaged that other material properties such as fracture toughness, a parameter relating to Young's modulus, may provide further understanding of the formation of non-cracking HC film formation in the future.

## Experimental Section

*General Procedure for Synthesis of Star Polymers*: The $\beta$-CD-based initiator (1 equiv.), PMDETA (1 equiv.) and monomer(s) (varied number of equiv.) (refer to ESI) were dissolved in toluene in a Schlenk tube. The mixture was subjected to three freeze-pump-thaw cycles and then backfilled with argon. The mixture was frozen in liquid $N_2$ and then CuBr (1 equiv.) was added under an argon flow. After a further three freeze-pump-thaw cycles and backfilling with argon the tube was sealed and the mixture was stirred at room temperature for 10 min followed by heating at 60 °C for 10 h. Detailed synthesis and characterisation of all polymers are provided in the ESI.

*Planar and non-planar HC Casting*: HC films were prepared by first stabilising the conditions of the casting environment to ca. 30 °C and 70 ± 5% RH. The star polymer was dissolved in chloroform (5 mg $mL^{-1}$) and 20 μL of the solution was then dropped carefully onto a circular glass cover slip (planar surface) or a TEM grid placed on a glass cover slip (non-planar surface) and the solvent and water left to evaporate.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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