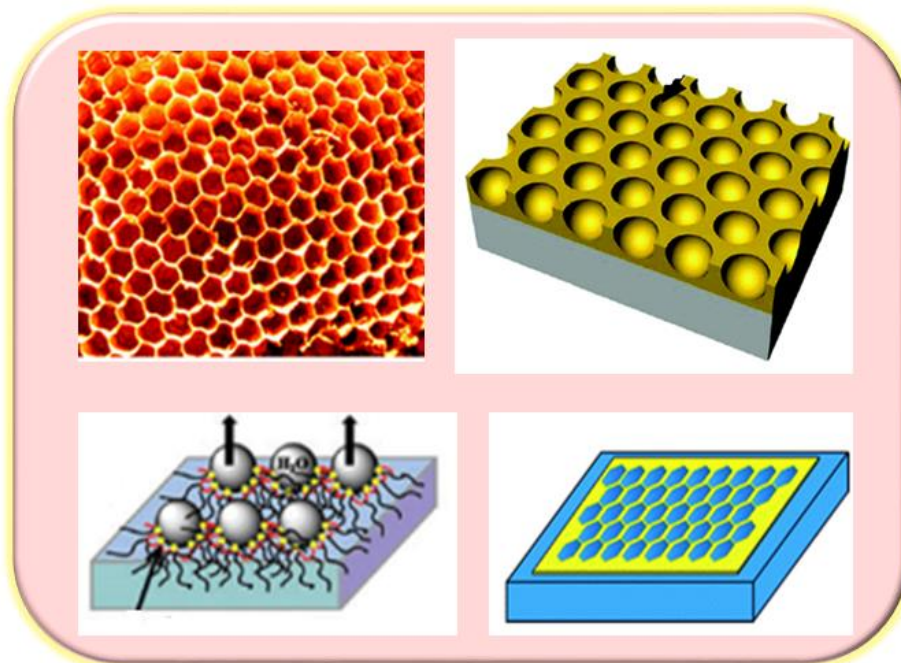


MICROPATTERNED POLYMER FILMS- AN OVERVIEW



1.1. INTRODUCTION

Porous polymers have received special interest in different industrial and research fields owing to their potential to merge the properties of both porous materials and polymers. The prime advantage of porous polymers is that they can be designed to high surface area, high porosity, etc. Moreover, easily processable in the monolith form or even as a thin film which has more practical applicability. Polymeric materials are easily soluble in different solvents and hence, porosity can be created directly using solvent based techniques (*Budd et al. 2004; Ghanem et al. 2008*). Moreover, vast varieties of fabrication routes are reported for porous polymers and enable the incorporation of multi-functionalities into the polymeric porous framework (*Rzayev et al., 2005; Hu et al., 2006; Ghanem et al., 2008*). These additional functionalities in the porous framework can provide stimuli-responsive

characteristics to the porous polymeric materials (*Li et al., 2008*). Another significant advantage of porous polymers is that they are of light weight, which facilitates them to be used in many applications (*Li et al., 2010*).

Porous polymers find wide range of applications such as gas storage (*Wood et al., 2008; Du et al., 2011*), separation materials (*Budd et al., 2010*), support for catalysis (*Pierre et al. 2006; Chan-Thaw et al., 2010*), sensors (*Zhao et al., 2007*), encapsulating agents for controlled release of drug (*Duan et al., 2005*), photonic band gap materials (*Huang et al. 2010*), low dielectric constant materials (*Hu et al., 2008*), template for replication (*Tseng et al., 2009*), materials for nano-patterning (*Park et al., 2008*), lithography, electrode materials for energy storage application (*Liu et al., 2008 ; Kou et al., 2011*), etc. These wide varieties of application demand consistent processing techniques which produce specific pore framework or architectures, sometimes contain additional functionalities.

There are three frequently used synthetic methodologies for the fabrication of porous polymers such as templating method (*Thomas et al., 2008*), block copolymer self-assembly (*Hillmyer, 2005*) and direct synthetic methodology (*Jiang et al., 2010*) which on expansion and further development leads to numerous processing techniques. In addition to this, internal phase emulsion polymerization (*Kimmins et al., 2011*), interfacial polymerization (*Li et al., 2010*) and breath figures techniques (*Bunz, 2006*) etc. have also emerged.

The direct templating method is a casting or molding technique in which a replica of the template is formed with stable morphology. Different pore geometries like spherical, tubular and ordered pore structures are produced in this methods. (*Martín et al., 2009; Decher et al., 1991*). Self-assembly of block copolymer (BCP)

opens another tactic approach to form well ordered meso and macro porous polymeric architectures (*Olson et al., 2008*). Block copolymers suitable for self-assembly are more than one immiscible hybrid macromolecules that are linked covalently. The thermodynamic incompatibility between the segments leads to phase separation to minimise their contact energy but not more than nano meter scale due to the chain connectivity (*Kim et al., 2010; Wan et al., 2008; Wang et al., 2011*). A number of diverse mechanisms can be chosen for the pore formation from the self-assembled BCPs. One among them is the selective etching of one component from the self-assembled BCP (*Mao et al., 2005; Zhou et al., 2006*). The phase separation of self-assembled BCPs in a suitable solvent is another sacrificial free method (*Wang et al., 2011; Wittemann et al., 2007; Park et al., 2008 ; Sun et al., 2009 ; Park et al., 2012*).

1.2. Micropatterned Polymer Films

Micropatterned polymer films are a class of porous polymeric materials which consist of uniform and ordered array of two or three dimensional micro-architectures. They possess many remarkable properties which are not the characteristics of the matrix materials but created due to the presence of the patterns. These materials have great importance in different area of modern science and technology with a wide range of applications such as optical and storage devices, photonic band gap materials (*Menard et al., 2007; Love et al., 2005*), catalysis and membranes (*Maschmeyer et al., 1995*), templates (*Connal et al., 2006*), protein arrays and (*Zhang et al., 2007*) cell culture scaffolds (*Tanaka et al., 2006; Beattie et al., 2006*), etc. However, the synthesis of micropatterns with controlled morphology remains a challenge. Recent developments in the fabrication of micro

and nano patterned surfaces with features and lateral dimensions includes lithography (*Geissler et al., 2004*), soft lithography (*Moran et al., 2008*), templating method (*Chen et al., 2003*), emulsions (*Imhof et al., 1997*) and self-assembled copolymer (*Stoykovich et al., 2005*).

In lithographic technique which is a conventional top-down technique, the substrate to be patterned is covered with a layer of radiation-sensitive polymer called a photoresist and then it is exposed to radiation so that the structure of the polymer is modified. After exposure, the resist polymer is developed in a suitable solution and the desired patterns are created on the substrate. Lithographic techniques are of different types such as photolithography, beam lithography, soft lithography (*Kon et al., 2010*), etc. Li et al. fabricated 2D nano array of ordered and non-spherical structures by the electron irradiation of polystyrene monolayer colloidal crystals followed by thermal decomposition (*Li et al., 2008*). Soft lithography offers advantage over other conventional lithographic method due to its low cost, simplicity, and ease of accessibility. In soft lithographic method, a pre-patterned elastomers usually made up of PDMS is used to generate patterns on the polymer film surface (*Xia et al., 1998*). Therefore, the mold should be patterned before it can be used as a template through other conventional lithographic techniques and limits the intrinsic advantages of soft lithographic methods.

The self-assembly process which is a template-free method leads to stable and well defined micro/macro patterns by phase separation of block copolymers. The phase separation can be achieved by various ways such as wet casting (*Shojaie et al., 1994*), dry casting (*Young et al., 2002*), vapour induced phase separation and thermally induced phase separation (*Teramoto et al., 2004; Altinkaya et al., 2004*).

The templating methods were developed to create micro/submicron dimension patterns with a wide varieties of approaches like ordered array of colloidal particles (Li et al., 2010), polymer spheres (Xue et al., 2008), emulsion droplets (Pietsch et al., 2009), self-organized surfactants (Zhang et al., 2010), etc. Most of the above mentioned process required a template removal procedure after the fabrication process. The synthesis and elimination of these templates are rather difficult (Tanev et al., 1994; Meng et al., 2002). This gave way to Breath figure (BF) method which exploits the natural templates of ordered array of water droplets and can be easily removed by simple evaporation process.

1.3. Breath Figure Method

The Breath figure (BF) method, which is an alternate form of templating method, opens a new era for the fabrication of honeycomb (HC) or micropatterned polymeric films with controllable pore over a large area. The versatility of this method lies in the usage of a dynamic template which is the ordered array of water condensate that can be removed by simple evaporation. Therefore, the use of specially designed template can be avoided thereby lowering the production cost. In addition, the self-removal of template reduces the production time. Another advantage of BF method is the employment of a wide variety of polymer or even hybrid composite thereby increasing the diverse applicability of this technique. (Hernandez-Guerrero et al., 2012 ; Muñoz-Bonilla et al., 2014).

The literal meaning of 'Breath figures' is the periodic structures formed by the exhaling of fog on a cold surface. The investigation on the formation of water droplet on cold surface was first done by Aitkek in 1911 followed by Rayleigh in 1911 (Aitkek, 1911; Rayleigh, 1911; Rayleigh, 1912). These water droplets nucleate

and organize on the cold surface by further condensation. They are stable initially but as time goes get collapsed with the neighbouring droplets (*Sokuler et al., 2010*). Later, Knobler and Beysens found out that breath figures can also be formed on liquid surface, especially paraffin oil. (*Knobler et al., 1988*).

The first attempt was done by Francois and co-workers in 1994 (*Widawski et al., 1994; Pitois et al., 1999*). They prepared self-assembled honeycomb structures of star polystyrene (SPS) and poly(para-phenylene)-block-PS (PPS) by exposing the drop cast of CS₂ solution of both to a moist air flow. They proposed a 'Marangoni-type convection of condensing water' and established that SPS and block copolymer like PPS are suitable for stabilizing water droplets and patterns with 0.2-10 μm size are assessable. Following this report, Jenekhe and Chen synthesised highly ordered honeycomb structure from polyquinoline-PS block copolymer with bubble sizes ranging from 2-4 μm (*Jenekhe et al., 1999*). These materials find application in device-type materials. The independent works of Srinivasarao and Han on carboxy terminated unmodified PS using carbon disulphide and chloroform solvent leads to an ordered breath figure pattern (*Srinivasarao et al., 2001*).

1.4. Mechanism of Breath Figure Array Formation

The exact mechanism for breath figure formation is not reported in much detail though slightly different mechanisms were proposed for each class of polymers. The overall process of breath figure formation can be summarised as follows: (a) the endothermic evaporation process of the drop cast of a polymer solution surface experiences a cooling effect. This allows the water vapour from the atmosphere to condenses on the solution surface in the form of droplets, nucleate and grow over time. (b) These nucleated water droplets are thermodynamically

stable due to their small size and hexagonally arranged on the polymer surface. (c) In the final stage, the temperature rises to the ambient condition accompanied by the precipitation of the polymer around the water droplets. The whole solvent and the water evaporates off leaving the hexagonal imprint of the water droplets (Muñoz-Bonilla *et al.*, 2014). Figure 1.1 depicts the experimental set-up for breath figure pattern (adopted from (Hernandez-Guerrero *et al.*, 2012)).

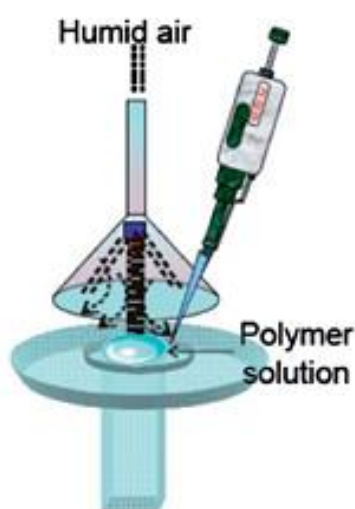


Figure 1.1. Experimental set-up for breath figure formation

Later on, many generalizations were developed to explain the formation and stabilization of breath figures on the polymer solution surface. Srinivasarao *et al.* (Srinivasarao *et al.*, 2001) developed an attractive mechanism for the breath figure pattern based on the formation and subsequent 'crystallization' of BFs. When a humid air passes over the drop cast polymer solution, rapid solvent evaporation occurs. This endothermic process reduces the temperature of the polymer solution to $-6-0^{\circ}\text{C}$ and induces subsequent condensation of water droplets onto the surface. These isolated water droplets float on the organic solvent nucleate and grow in size over time. After that, these non-coalescing droplets get organised in a hexagonal fashion and form a 'quasi-crystalline' mobile array of water droplets.

These droplets may sink into the polymer solution so that polymer get precipitated at the interface. After the complete evaporation of solvent and water, an imprint of the hexagonal array of water droplet forms on the polymer surface. Sometimes, the sinking of the first layer of water droplet creates a fresh layer of polymer solution above it where a second non-coalescing mobile array of water droplet might have formed. Thus, the imprint of water droplet creates a 2D or 3D (multi-layered) porous structure on the polymeric material (Figure 1.2)(adopted from (Srinivasarao *et al.*, 2001).

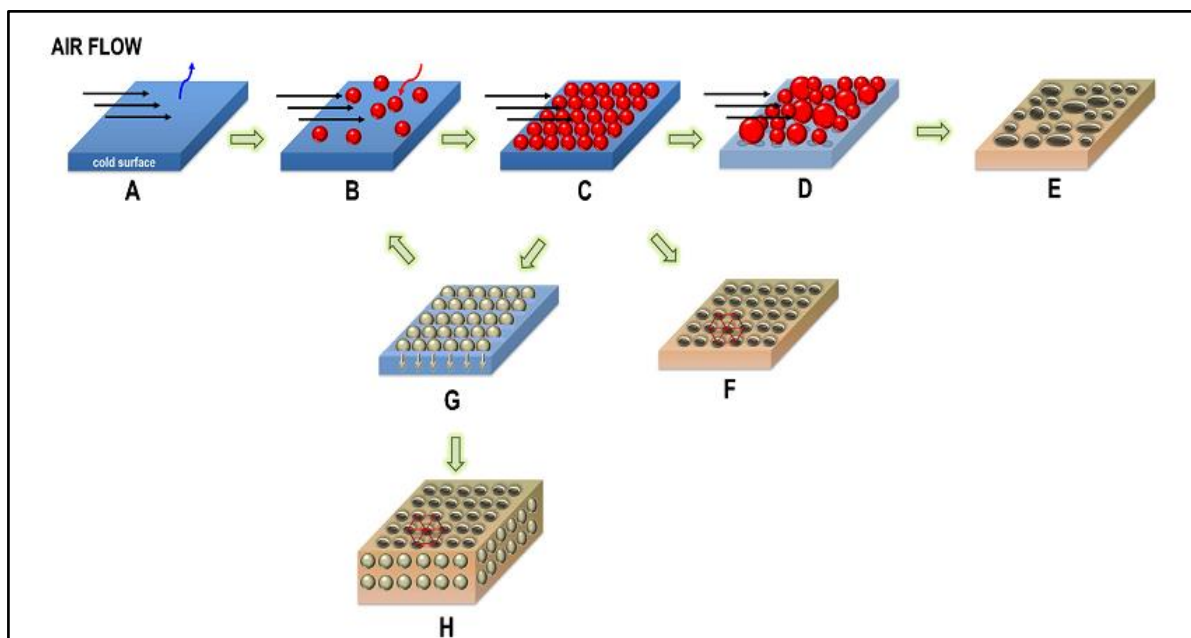


Figure 1.2. Schematic representation of breath figure pattern formation

As mentioned above, breath figure method allows the formation of either a monolayer or multilayer of pores and the density of the solvent plays a key role in this decision. A monolayer of pores is favoured by solvents that are less dense than water. The condensed water droplets on the polymer solution surfaces are stabilized by the precipitated polymer around the interface and less dense solvent facilitates the easy sinking of these water droplet into the polymer solution.

Although this is a general observation, some exceptions are found, that is, CS₂ even though denser than water favours monolayer of patterns.

Mono/multilayer formation is affected by yet another parameter, the film thickness. It is observed that the cast film of thickness 250 μm forms monolayer, thickness ~500 μm forms partial multilayer and thickness 1000 μm forms a complete double layer of self-assembled pores. Another attribution is relating the porous structure with the interfacial interaction between polymer, solvent and water according to the following empirical formula (*Bolognesi et al., 2005*).

$$Z_0 = \frac{\gamma_w - \gamma_{w/s}}{\gamma_s}$$

Where γ_w is the surface tension of water, γ_s is the surface tension of solvent, and $\gamma_{w/s}$ is the water/ solvent interfacial tension. According to this model, a multilayer is formed when z_0 is higher than 1. When z_0 value is between -1 to 1 droplets floats at the air solution interface and monolayer is formed. It seems that polymer concentration also plays a role in determining the mono/multilayer formation. As the concentration increases, multilayer is transferred into the monolayer.

Many contradictory explanations exist for the non-coalescence of water droplets of breath figures. Srinivasarao and his co-workers' theory was based on the thermocapillary effect combined with Marangoni convection which stabilizes the water droplets from coalescing. Thermocapillary effect is the temperature gradient induced motion of one liquid in another one when both being immiscible (*Schatz et al., 2001*). Here the air/solvent interface acts as one liquid and in such case there is negligible possibility for miscibility of the liquid droplet of identical materials. Another factor which prevents coalescence is the Marangoni effect in which two

identical liquid droplets will not collapse together until a sufficiently large temperature gradient exist.

Shimomura et al. proposed that the water droplets do not levitate on the solvent in any ordered arrangement initially, but the thermocapillary effect and Marangoni effect make the water droplet submerge into the organic solvent and are responsible for the hexagonal arrangement of water droplets (figure 1.3.) (Maruyama et al., 1998). But in the final stage the water droplet stabilization occurred by the precipitated polymer layer around the droplet which act as a 'polymer bag' and solidifies the bubble array (Pitois et al., 1999). As the solvent evaporation continues, the viscosity of the polymer solution is increased which locks droplet array. An open pore structure is formed if the connecting polymer skin is too thin.

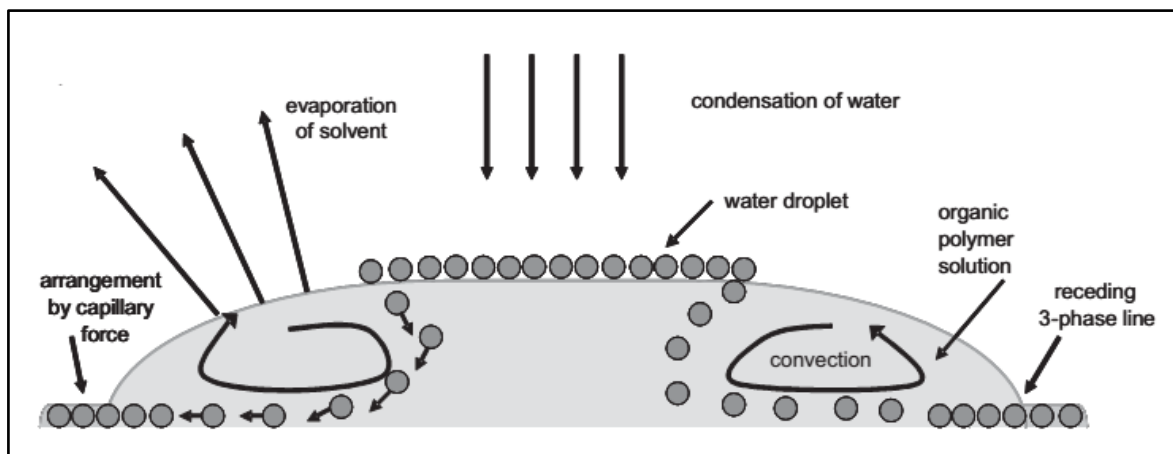


Figure 1.3. Mechanism of breath figure formation and the arrangement of water droplets into hexagonal array by thermocapillary and Marangoni effect

Many studies have been done on the kinetics and dynamics of bubble nucleation and growth on the solid surface. According to Steyer et al. (Steyer et al., 1990), bubble growth depends on time and varies linearly with various exponents of time at the three different stages of breath figure formation. At the initial stage,

the droplet diameter D is directly proportional to time 't' according to the power law $D \sim t^{1/3}$, as there is no strong interaction between droplets. The next stage which is a 'crossover' stage, the droplets are separated by a thin liquid film, and the whole surface has a maximum coverage of droplets. The final stage which can be called as a coalescence domination stage, the surface coverage is high and constant. Here the droplet growth is also high according to the equation $D \sim t$ (Figure 1.4. adopted from (Muñoz-Bonilla et al., 2014)). Not only the coalescence, but the boundary conditions of the droplet also influences the droplet growth in BF pattern. So introducing this parameter a new model was proposed called the 'similarity variable approach' or 'quasistatic approximation.' A universal law has been put forwarded for droplet growth at long-time limit based on the relation $D \sim (t/\ln(t))^{1/3}$. (Fritter et al., 1991; PL, K. et al., 1993).

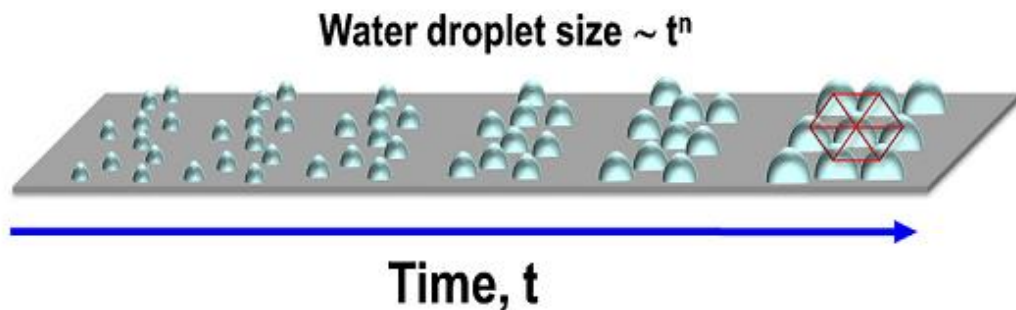


Figure 1.4. Water droplet growth as a function of time

Based on the theoretical study of the BF pattern formation on polymer solution, Billon et al. (Billon et al., 2009) interpreted various factors which could influence the droplet diameter such as polymer concentration, nature of the solvent, temperature, air flow rate, etc. They summarised that the pore diameter decreases linearly with polymer solution concentration and the BF patterning strongly depends on the characters of organic solvents. They also stated that rapidly evaporating solvent induces a good organization of water droplet array but get

destroyed when the substrate is heated from below. Contradictory to the temperature-gradient-Marangoni effect this theory predicts a concentration-gradient-driven effect for the self-organization.

1.5. Factors Affecting Breath Figure pattern

The structure of BF patterns depends on many parameters like humidity, solvent, temperature, concentration, polymer architecture, its molecular weight, polymer-solvent interaction, etc. These factors can be effectively utilized to tune and optimize the pore size, shape, and pore density of the BF pattern.

Humidity

A humid atmosphere is an essential experimental condition for the formation of BF pattern. A favourable environment for the formation of good BF pattern should have a relative humidity of 50% or higher. Even the regularity and size of pores can be optimized by fixing a suitable humidity condition. A linear increasing trend of pore size with humidity is observed. However, high humidity leads to vast condensation and increases the coalescence of water droplets resulting in polydispersity in the patterns.

Solvent

The choice of solvent is the most important parameter for the formation of regularly arranged BF pattern as it is driven by the features like high vapour pressure, low boiling point, low solubility in water and a higher density than water. Solvents like carbon disulphide, chloroform, dichloromethane, benzene, toluene, THF, freon, etc. or their mixture are most commonly used for BF technique. CS₂ and CHCl₃ are best among them for the formation of regular BF patterns due to their peculiar features.

The casting process and the condensation of water droplets are highly influenced by the evaporation rate of the solvent. Moreover, the solvent determines the conformation, surface tension, and viscosity of the polymer solution, which affects the final structure. A multi layered porous structure is preferred to form at low evaporation rate because the droplets get enough to sink into the polymer solution and allowed the second layer to be condensed on the newly created solution surface before the complete evaporation of the solvent (*Billon et al., 2009*).

Concentration

BF morphology and the mono/multi-layer formation is also affected by the polymer concentration. As the concentration of the solution increases monolayer converts into multilayer as the viscosity of the solution influence the sinking of the droplets. There is an inverse relation between pore size and polymer solution concentration according to the equation, $D = (k/c)$, Where 'D' is the pore size, 'k' is a constant that depends on the type of the polymer and 'c' is the concentration of polymer solution (*Stenzel, 2002*).

Air Flow

A lower air flow rate reduces the evaporation time and allows growth of the water droplet and results in bigger pore size. Higher evaporation rate decreases the pore size. So air flow rate can be altered to tune the pore size of BF pattern.

Polymer Structures

Although no empirical relation exists between polymer structures and pore size, some polymers show feasibility to be self-assembled at the interface. Different polymeric structures like star polymers, block copolymers, amphiphilic polymers, etc. could create regular BF patterns. For example, star and hyper branched

polystyrene gives regular BF patterns whereas linear polystyrene failed to achieve any regular pattern. Modification of a star polymer by increasing its arm would increase the segment density, and this behaves as a strong 'end-group'. This stabilizes the water droplet by its strong arm and thereby reducing the pattern size. 18-arm cyclodextrin based star polystyrene can create BF pattern with a cavity size of 250 nm (*Stenzel-Rosenbaum et al., 2001*) and the pore size increases as the number of arm decreases.

Polymer with a polar end-group could stabilize the BFs and help to produce regular patterns. These polar groups on the polymer extend towards the water phase and prevent the droplet from coalescence. For example, although linear polystyrene is not a BF compatible polymer, terminal carboxylate group on the polymer can generate regular patterns under suitable casting conditions (*Bolognesi et al., 2005; Stenzel et al., 2006*). Similarly, highly ordered honeycomb films were fabricated using linear polystyrenes of low molar mass ($M_n = 20,000 \text{ g/mol}$) with chain end containing ionomers by Billon and his co-workers (*Billon et al., 2009*). In the organic solvent these ionomers self-assembled into inverse micelle and resembles a star-like polymeric structure. However, the polar end group should have the capability to stabilize the water droplets. For example, carboxy-terminated star PS forms good BF patterns in carbon disulphide, whereas ester terminated PS does not give such regular array of patterns.

The ability of block copolymer to stabilize the BFs was utilized by Lord et al. by preparing regular BF array from a cross linked star polymers of styrene and divinylbenzene. The pore size and regularity of the patterns depends on the crosslinking time and molecular weight of the arms (*Lord et al., 2003*). Amphiphilic

block copolymers prepared by crosslinking acryl phosphocholine into a PS block copolymer forms ordered BF patterns with cavity size of 2-3 μm . Here the pore morphology mainly depends on the polar to non-polar balance.

Several groups attempted to improve the property and the stability of patterned films to make use of them under different environmental conditions. B. Erdogan et al. (*Erdogan et al., 2004*) prepared micropatterned structures useful for electroanalytical and bioanalytical applications in picoliter wells from the conjugate polymer azide PPE by crosslinking in air at a temperature above 280 $^{\circ}\text{C}$. Heating instead of melting make the polymer softened so that pores with interconnectivity get collapsed into insoluble cup-shaped holes called picoliter beakers. Shrinking occurs in the z direction with pore size reduction from 4 to 1.5 μm , but shape persists in x-y direction (Figure 1.5.)

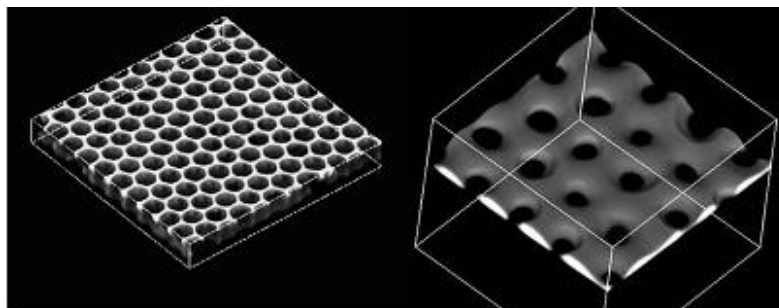


Figure 1.5. 3D reconstruction utilizing scanning confocal microscopy of a bubble array of azide polymer cast from CS_2 (reprinted from (*Erdogan et al., 2004*))

Similarly, highly crosslinked ceramic patterns were synthesised by B. Englert et al. (*Englert et al., 2005*) based on organometallic PPE materials. The BF patterned film formed from the casting of CS_2 solution of the above material on heating above 600 $^{\circ}\text{C}$ do not melt but gave a crosslinked insoluble patterns. Due to the high pyrolysis temperature these materials are ceramic in nature, not merely organic. I.

A. Bashmakov et al. (*Bashmakov et al., 2002*) fabricated metallized carbon networks by treating the cast from amyl acetate solution of carboxylated nitrocellulose with Ni (II) acetate or Co(II) acetate in water. Ion exchange occurs without disturbing the pattern and the pyrolysis at 700 °C gave 2 μm sized honeycomb structures with 25 % ceramic yield.

Cross-linked micropatterned surface from four armed star poly (D,L- lactide) end modification with 2-isocyanatoethyl methacrylate has been fabricated by Karikari et al. (*Karikari et al., 2006*). The film was photo-cross linked by UV radiation, using the photo initiator 2, 2-dimethyl-2-phenol acetophenone which was added in the polymer solution prior to pattern formation. A self-cross-linking mechanism was operating for star polystyrene-b-polybutadiene honeycomb by exposing to UV light in air at 30 °C (*Xiong et al., 2011*). Chemical reaction induced property improvement in the patterned film was achieved by Kabuto et al. (*Kabuto et al., 2007*). They prepared thermally stable and solvent resistant HC films based on poly(styrene-co-maleic anhydride) by immersing HC film in ethanol solution of α, ω-alkyldiamine thereby inducing a post chemical reaction. Another strategic method for property refinement was done by Wong K. H. et al. (*Wong et al., 2010*) by developing flexible, thermally stable (up to 85°C), and organic solvent resistant patterned structures based on methacrylic branched copolymers containing alkoxy silane-based co-monomer which can promote the cross-linking via sol-gel process using triethylamine acetonitrile/water solution as a catalyst. Even non-soluble polymeric BF patterned films were synthesised by thermal treatment of polyfluorene co-polymer with side chain protected by tetrahydropyranyl residues (*Bolognesi et al., 2010, Li et al., 2011*).

The above reports suggests that a vast variety of polymers can be employed for breath figure formation. However, there should be a water droplet stabilizing moiety to improve the regularity of the patterns. In addition, the morphology and property refinement is possible either by the pre or post modification of the polymer or by altering the physical and chemical BF environment.

1.6. Different Fabrication Methods for Breath Figure Formation

The typical procedure for the BF formation includes the casting of polymer solution on a suitable substrate under a humidity greater than 50%. However, some modification were adopted to improve the regularity and to tune the pore morphology as represented by figure 1.6. For example, control over the solution temperature can alter the condensation rate of water droplets, evaporation rate of solvent, and also the viscosity of the solution, thereby changing the morphology of pattern.

i) Simple Casting

The polymer solution in a suitable solvent is casted on a substrate and the solvent is allowed to evaporate off in open atmosphere. The various environmental factors affect the BF morphology as the drying was performed in open atmosphere. The humidity of the atmosphere should be more than 40-50 % for the uniform formation of the pattern.

i) Air Flow Technique

In this method a moist air flow is passed over the polymer solution cast which rises the solvent evaporation rate and thus provides a large temperature gradient between the surface and bulk of the cast. An added advantage is that it promotes the convection in the solution thereby regulating the arrangement of

water droplets. The key factors which influence the pore characteristics are the air flow rate, distance between the airflow source and the polymer cast and the angle of the air current. (Yabu *et al.*, 2003).

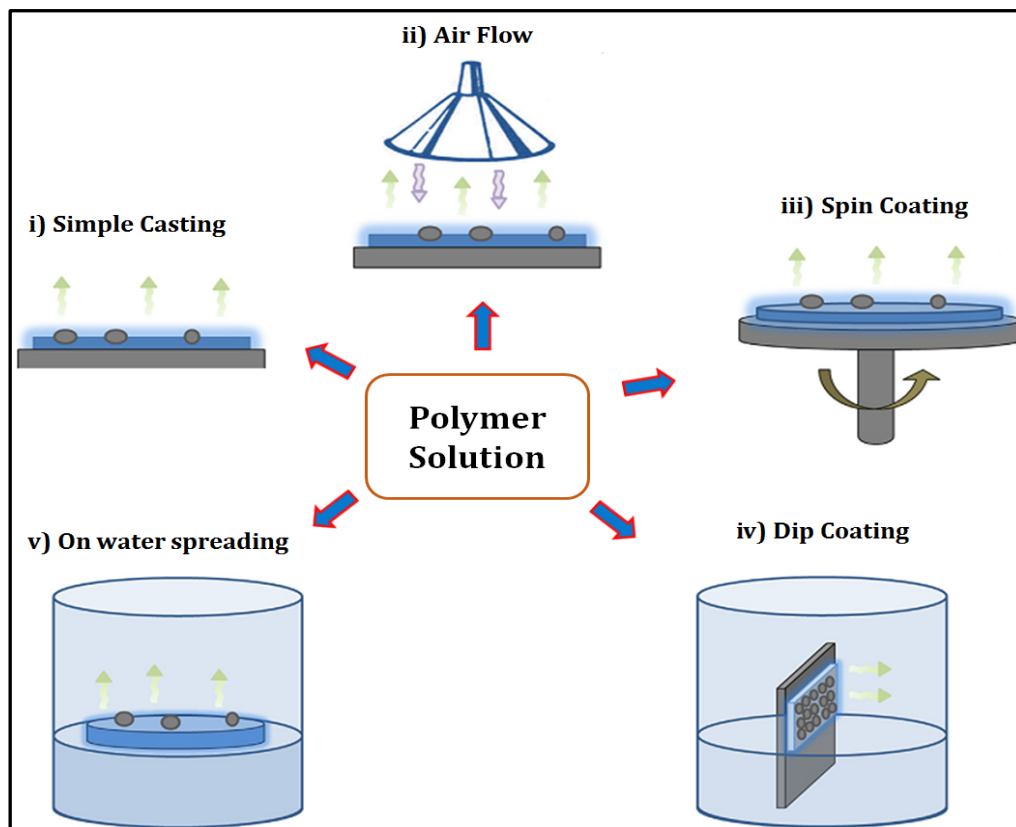


Figure 1.6. Representation of instrumental set up for the preparation of BF films via various process (adopted from (Muñoz-Bonilla *et al.* 2014))

ii) Spin Coating Method

Spin coating is a versatile technique used in combination with breath figure method for the preparation of uniform thin films with BF patterns in a large area. In order to achieve the desired humidity condition, beakers containing hot water can be placed inside the spin coating chamber (Pilati *et al.*, 2007). The pore characteristics were tuned by different spin rates, i.e. a higher spin rate generates regular porous structures with small size whereas low spin rate leads to large and

irregular arrangement of pores. Unlike the airflow technique, spin coating produce elongated pores rather than spherical.

iii) Dip Coating method

In this method, BF patterned polymer film is prepared by dip coating and allowed for solvent evaporation. Because of the vertical position of substrate the sinking of water droplet is not due to gravity, but through some interfacial forces which controls the movement of water droplets and the polymer solution.

iv) 'On water spreading' Method

Self-supported porous polymer films can be fabricated by spreading a polymer solution on air/water interface. Amphiphilic copolymers are good candidates for this approach and the pioneer work in this respect was done with amphiphilic polyacrylamide (*Nishikawa et al., 2002*). After the complete evaporation of solvent, the polymer film is transferred into a glass slide and dried. The pore size of the BF patterned film depends on the amount of the casted polymer solution whereas the temperature of the bath mainly influences the film thickness and the density of pores.

v) Emulsion Technique

As the name implies this method uses water-in-oil system for fabricating BF structures. i.e. water is directly added into the polymer solution and homogenized by sonication. Water miscible solvent like THF are more desired for this type of processing technique (*Kasai et al., 2004*).

1.7. Different Approaches to Modify the Pore Morphology

Many strategies are developed for the modification of pore morphology using mechanical forces like shrinking, stretching, variation in the orientation of air flow

during condensation, usage of template to form complimentary structures and peeling off the first layer to form pin cushion like structures. The different morphologies were shown in figure 1.7. (Muñoz-Bonilla *et al.*, 2014)

The shrinking method can be employed to modify the size as well as the shape of the pattern. Shrinkable polymers are employed for this type of modification. Initially, the polymer is stretched for BF formation and then heated above its glass transition temperature so that it shrinks due to entropic relaxation (Yabu *et al.*, 2008). Stretching can be achieved in viscoelastic polymers and a topology equivalent to hexagons, elongated hexagons, rectangles, square and triangles can be created.

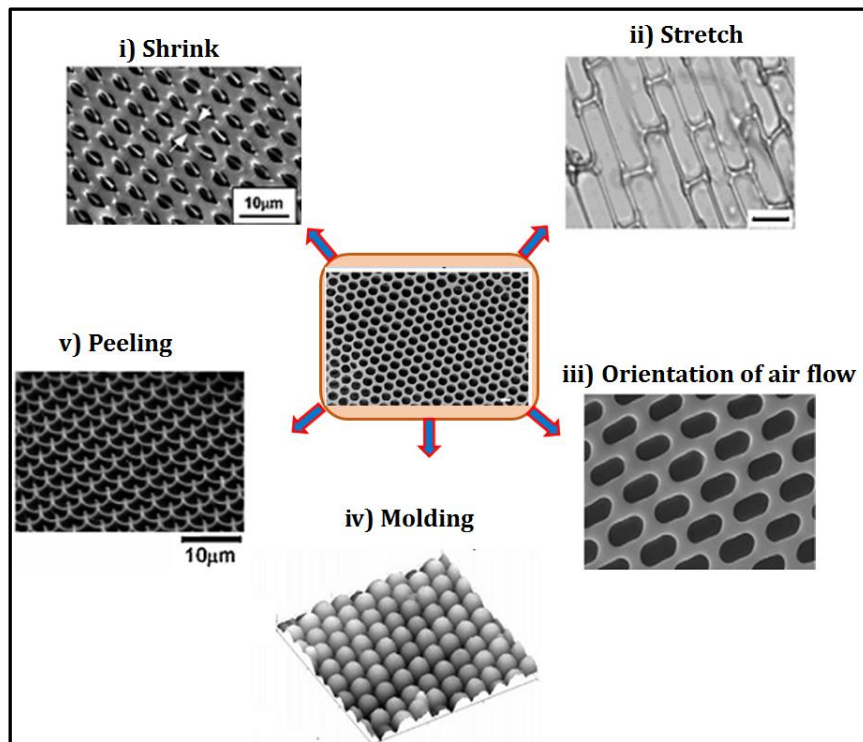


Figure 1.7. Schematic representation of various approaches for the modification of pores

Pore characteristics can be modified by changing the orientation and velocity of air flow. Circular BF cavities are obtained when air flows normal to the surface of

polymer cast while shape tends to be elliptical with airflow at an angle of 15° with respect to the solution surface and the aspect ratio of the ellipse can be altered by changing the velocity of the air flow. In molding technique, a replica of the honeycomb structure is produced. Peeling is yet another method which produces pincushion structures by peeling off the surface of the honeycomb.

1.8. Functionalized Breath Figure Cavities

The applicability of micropatterned polymer surface can be improved by introducing additional functional group inside the pores such that films with functionalized pore could be useful for micron sized reactors, the design of sensors, filters, catalytic sites, etc. (Connal *et al.*, 2010; Ke *et al.*, 2010) However, the design and control of the functional group inside the BF cavity involves some crucial processes. There are possibilities for '*in-situ*' and '*ex-situ*' functionalization of pore cavity. Figure 1.8 represents the different methods to obtain functionality inside the breath figure cavities.

Functionality can be introduced '*in-situ*' by simple casting of the functional homopolymers, amphiphilic polymers or organic/inorganic hybrid polymers. Simple functional polymers produce honeycomb structures in which the functionalities are homogeneously distributed. Complex structured homopolymers like star polymer are used to form regular BF structures (Widawski *et al.*, 1994). An added value is obtained to these structures when functional polymers or polymers with special properties are used. For example, polyimides are thermally and chemically stable polymers and can lead to patterned microporous films. BF structures from natural polymers like cellulose derivatives can be used as cell

culture substrate because of their biocompatibility and mechanical strength (Kasai et al., 2004).

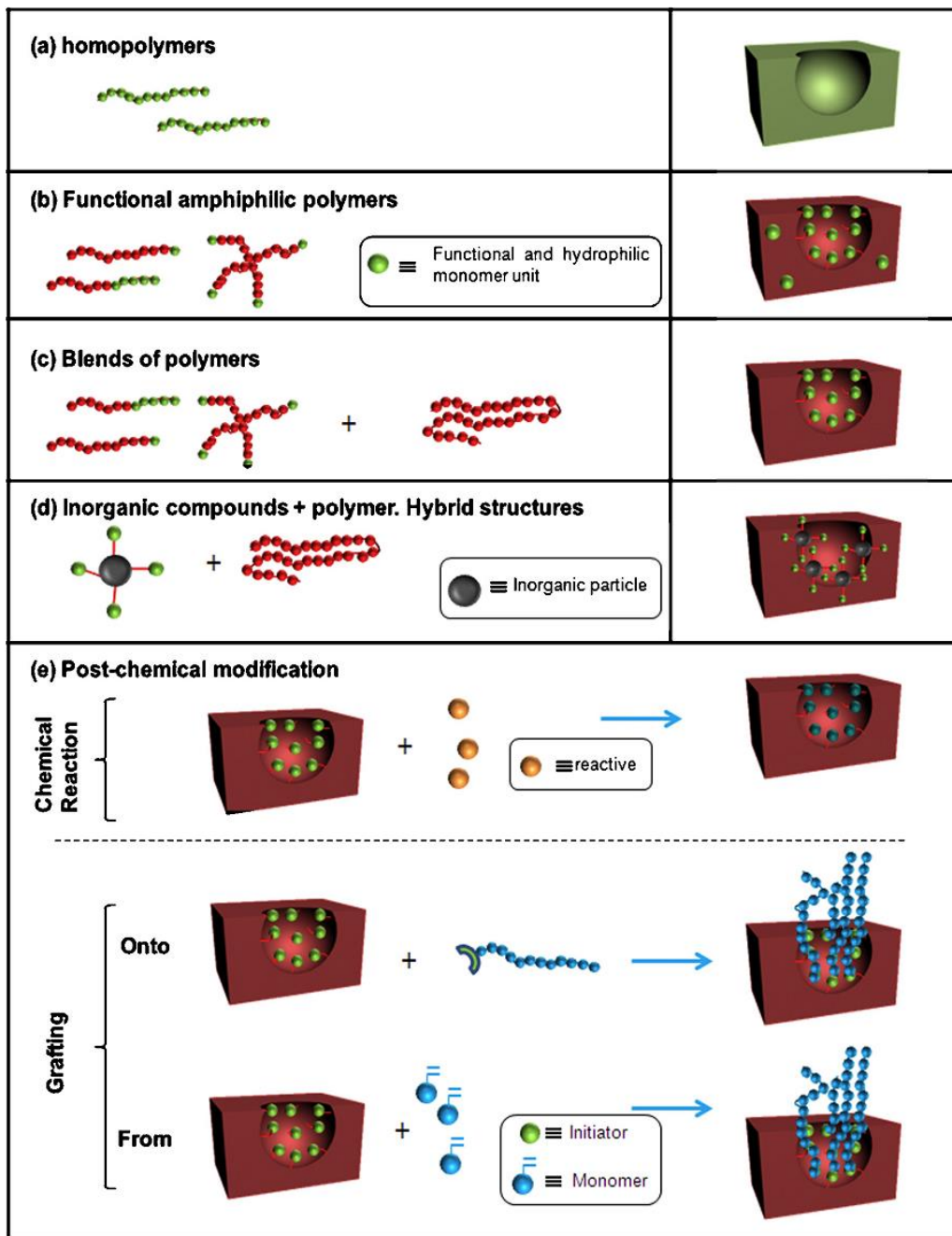


Figure 1.8. Different methods to enrich functionalities inside the breath figure cavities

In the case of BF formation with amphiphilic copolymers, the crucial step is the designing and generation of the chemical functionality in a single process. The BF patterns in amphiphilic polymer films are specially decorated with the

hydrophilic functional groups aggregated in the wall of the cavity. Linear polymers with functional end are synthesised by 'living' polymerization technique. Yunus S. et al. (*Yunus et al., 2007*) has synthesised 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) terminated polystyrene for which the end group was converted into p-toluenesulfonate piperidinium through Nitroxide-mediated radical polymerization. These polar groups present on the PS leads to the ordered BF formation with cavities functionalized with these end groups which was confirmed by fluorescent indicators. Ionomers are introduced as functionalities on hydrophobic polymers and copolymers by a one-step polymerization reaction using nitroxide-mediated cationic or anionic initiators by Billon et al. (*Billon et al., 2009*). The carboxy-terminated polystyrene forms BF patterns only in the deprotonated form confirms the importance of amphiphilic character. In spite of the various works in polymers with polar groups, the most widely used materials for BF formations are amphiphilic block co-polymers. They contain more than one functional groups per molecules and the ability of micelle formation aids the stabilization of water droplets. Moreover, the hydrophilic to hydrophobic balance of the block co-polymers influenced the pore size, spacing and quality of the patterns.

Stenzel et al. (*Stenzel et al., 2003*) synthesised regular BF patterns on the drop cast film of a block copolymer based on polystyrene and poly (acryloyl phosphorylcholine) which functioned as the polar functional block. The X-ray photoelectron spectroscopy indicated the aggregation of these functional moiety around the pores. The amphiphilic block copolymers of polystyrene-b-poly(N,N-dimethylacrylamide) (PS-b-PDMAm) forms regular BF patterns by taking the advantages of reverse micelle formation which stabilize the water droplets either

by solubilizing water or by arranging around the water droplets. As a result, the pore interior was enriched with the hydrophilic blocks (*Wong et al., 2007*). Another example is the block co-polymer formed by PS and PS having 3,4-ethylenedioxythiophene oligomers as side chains. The polar fluorescence species, 4-ethylenedioxythiophene oligomers were located on the edge of the pores which was confirmed by fluorescence spectroscopy (*Bolognesi et al., 2008*).

Polymer blends are another suitable candidate for the synthesis of functional cavities since the functional polymer embedded into another polymer matrix entertain the preferential orientation of functionalities inside the pores. In addition polymer blends can improve the system integrity. Munoz-Bonilla et al. (*Muñoz-Bonilla et al., 2010*) fabricated patterned polymer surfaces from the blends of polystyrene and poly(styrene-co-((d-glucofuranosyl) aminocarbonyloxy) ethyl acrylate) glycopolymer with cavities walls decorated with the glycopolymer as a consequence of the interaction between polar glycopolymer and water droplets. Another group of researchers used amphiphilic ABS triblock copolymer of poly(2,3,4,5,6-pentafluorostyrene)-b-polystyrene-b-poly(poly (ethylene glycol) methyl ethermethacrylate) (P5FS-b-PS-b-PPEGMA) with high molecular weight PS and spin coated in the moist atmosphere (*Muñoz-Bonilla et al., 2009*) to produce patterned surfaces enriched with triblock copolymer. Another remarkable advantage of using the blend is that relative low amount of the functional polymer is required to obtain the patterned surface.

Moreover, micropatterning can be created on an incompatible homopolymer film surface by a combined procedure of breath figure method and phase separation. Xue et al. (*Xue et al., 2012*) proved the formation of BF pattern on

incompatible PS surface by incorporating poly(2-vinylpyridine) (P2VP), which can stabilize the water droplets because of its hydrophilic nature.

1.8.1. Inorganic Compounds and Polymer Hybrid Structures

Inorganic particles can be employed as a suitable candidate for the functionalization of BF pattern by a straightforward one step process. This can be done by dispersing or 'in-situ' generation of inorganic nanoparticles in a BF compatible or incompatible polymer. In the case of hybrid composites, the water droplets condense on the cool surface of the polymer solution can be stabilized by a layer of adsorbed inorganic nanoparticles. This was achieved by the fluid direct self-assembly of nanoparticles at the oil/water interface which otherwise called as the 'Pickering emulsion'. These particles act as a coalescence barrier for the water droplets (Sun et al., 2008). The complete evaporation of the solvent and water leaves BF cavities decorated with particles. However, the physical and chemical nature of the adsorbed particles influences the pore morphology.

Pieranski (Pieranski, 1980) theoretically described the behaviour of the colloidal particles at the interface by relating the energy required to remove the particles from the interface E as follows

$$E = \pi R^2 \gamma_{wo} (1 - |\cos \theta|^2)$$

Where 'R' refers to the particle radius, γ_{wo} represents the water/oil interfacial tension, ' θ ' is the contact angle measured through the water phase. For a given emulsion system, γ_{wo} and θ will be constant and hence the energy E depends on the radius of the particles. If the particle size is big enough, the value of E can be larger than the thermal energy $k_B T$. Therefore, the particles that adsorbed at the interface are more stable than the surfactant molecules and are better candidates

for stabilizing the BF interface. Although the adsorption energy increases with the size of the particles, there is no competitive preference based on the size of the particles to be adsorbed at the interface. Once the particles were adsorbed at the interface they will be transported along with the water droplets to the three phase contact line by the thermocapillary effect (Sun *et al.*, 2010). It is to be noted that small sized particles could move along with the water droplets more easily than the large particles and hence have a better chance to be embedded in the BF cavities.

The adsorption of nanoparticles or microparticles at the oil/water interface has a century-long history. However, an appropriate surface hydrophobicity of the particle is importance for the self-assembly of particles at the interface. Figure 1.9. demonstrated particle adsorption at the BF interface.

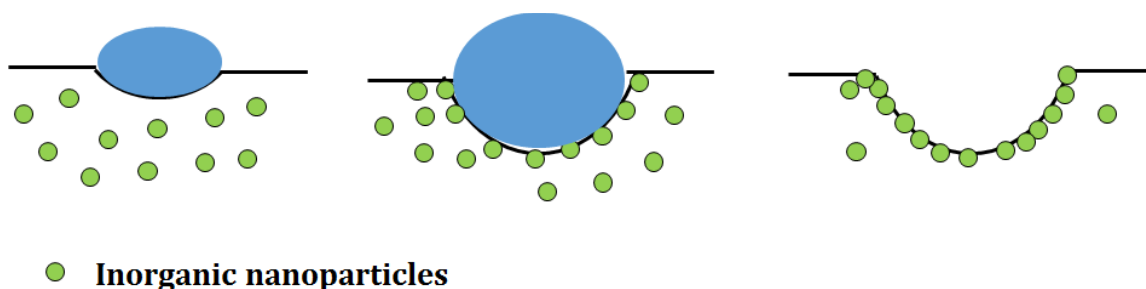


Figure 1.9. Schematic representation of attachment of inorganic particle at the breath figure interface

Saunders *et al.* applied pure nanoparticle systems in the BF method without any polymers and they obtained ordered macroporous nanocrystal film (Shah *et al.*, 2003; Saunders *et al.*, 2004). A prior approach for utilizing nanoparticles as a BF stabilizer was put forward by Russell and co-workers (Boker *et al.*, 2004). They fabricated hexagonal array of BF cavities on polystyrene film which were decorated with cadmium selenide (CdSe) nanoparticles. These particles were modified with Tri-n-octylphosphine oxide and form a uniform layer around the water droplet

interface. In the present system, the polystyrene used was BF compatible and the particles do not assist the breath figure mechanism, but functionalise the cavity.

Sun et al. clearly depicted the particle assisted BF mechanism by decorating a ring of nano silica particles at the BF interface of polymeric film. They combined the Pickering emulsion and capillary flow of particles in BF method (*Sun et al., 2008*). Templated self-assembly process for directing the nanoparticle to the BF interface is another strategy in creating hybrid patterned films. Nurumavati et al (*Nurumavati et al., 2008*) explored the novel features of tailor made conjugated poly (p-phenylene)s, (C12PPPOH)s as a template for the assembly of nanoparticles. Metallic nanoparticles like AuNP, carbon nanotubes, etc. were introduced into the chloroform-CS₂ solution of the polymer and casted on a substrate. The BFs were formed with cavities embedded with particles and the size of which decreased with the increase in the nanoparticle loading.

Hybrid thin film for optoelectronic application by multilevel organization of zeolite crystals on breath figure interface of an electro-luminant conjugated polymer was demonstrated by Vohra et al (*Vohra et al., 2009*). The influence of hydrophobic/hydrophilic balance of the zeolite crystals on stabilizing the breath figures array was studied and found that different functionalities on the zeolite surface led to different organization inside the cavities. The regular BF patterns formed on the aPS were disturbed by the presence of APTES modified Oxonine loaded zeolite crystals. Whereas, the regularity can be achieved by carboxylic acid functionalized oxonine loaded zeolite crystals for CS₂ solution of poly((9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1 0,3}-thiadiazole)) PF8BT.

Bo You et al. (*You et al., 2008*) introduced a novel method for fabricating ordered porous nanocomposite film with a water borne polymer poly (Styrene-co-butyl acrylate-co-acrylic acid). They prepared a dispersion of the polymer silica nanocomposite by emulsion polymerization, the solution was casted on a glass substrate and force dried at high temperature. The advantage of this process is that an ordered porous nanocomposite can be prepared from a water-borne system without the use of any solvent. Bindhu et al. (*Nair et al., 2010*) reported the formation of micropatterned polystyrene-clay nanocomposite (PCN) by moisture induced phase separation method. They proposed that the water droplets condensed on the polymer solution were channelled through the hydrophilic interfaces between the PCN particles and created a two dimensional concavities by spontaneous phase separation due to the presence of rigid clay platelets. They also demonstrated the BF morphology variation with solvent using chloroform and carbon disulphide.

Jiang et al. (*Jiang et al., 2010*) studied the interfacial effect of 'in-situ' synthesis of Ag nanoparticles on BF. They used polyurethane (PU) in THF/ethanol solution containing 1 % Ag nano particles and poly (L-lactic acid) (PLLA) in CHCl₃/ethanol solution contain 1% Ag nanoparticles by mixing the polymer solutions with AgNO₃ followed by reducing AgNO₃ with NaBH₄ to form Ag nanoparticles. At high humidity there is no apparent difference between pure polymer cast and PU/Ag nano composite. But Ag nanoparticles began to influence the BF process at lower humidity (30%). In the cast of PLLA, the pores are irregular but become regular in presence of Ag nanoparticles at high humidity. The influence of physical and chemical properties of the particles such as the particle size, wettability and

quantity to stabilize the BF interface in PS film was explained by Sun et al. They used hydrophilic and hydrophobic silica particles and used ethanol as a 'solvent surfactant' to disperse the particles in organic solvent. They found that the regularity of the BF pattern improved with the increase in the particle size (*Sun et al., 2010*).

The incorporation of inorganic nanoparticles to the patterned polymeric film enhanced the rigidity, mechanical strength, thermal and optical properties. These properties empowered the applicability of patterned hybrid films in biological, optical and various industrial fields. Wan et al. fabricated patterned bio catalytic film containing enzymes via one step self-assembly (*Wan et al., 2012*) based on the self-assembly of horseradish peroxidase (HRP) nanoparticles. HRP showed resistance towards organic solvents and the bio-hybrid film possessed robust catalytic activity. They observed that the BF cavity diameter increased with the quantity of the particles. Similarly, patterned multiscale bio-inspired hybrid films with high mechanical strength and low density was fabricated by Xu et al. (*Xu et al., 2012*) using polyamide (Mw= 26000-38000) as the base material and nano clay as the enhanced layer in the BF film. The orderly arrangement of pore increased with clay content until the saturation value of loading (0.9%) was reached. Moreover, the mechanical properties of the patterned hybrid films were greatly enhanced and increased with clay content.

Breath figure structures can also be used as a template for hybrid film fabrication to enhance the unique properties of the matrix material. Kon et al. reported the use of microporous polymer film for the preparation of porous zinc oxide film by casting Zn acetylacetonate/polymer solution at high humidity and

vacuum evaporated onto a preformed microporous polymer film. The organic material can be annealed to form the porous zinc oxide films. These films showed increased photocatalytic activity compared to the unstructured film (Kon *et al.* 2010). Another strategic application of the breath figure patterns aroused when Li *et al.* fabricated hemispherical or mushroom like micro titania particles (Li *et al.*, 2011). The colloidal particles with specific asymmetric structures and their assembly have unique photonic properties and have promising applications in photonics and other fields. Their group developed a bottom-up approach to fabricate patterned surface with asymmetrical TiO₂ micro particles trapped in the holes of the honeycomb polymer film from a solution of TiCl₄/PS/CHCl₃ by BF method. The shape of the particles can be tuned by adjusting the concentration of TiCl₄ and PS.

Another strategy for the development of functional honeycomb patterned films with controllable pore sizes via BF based on ionomers was demonstrated by Wang *et al.* (Wang *et al.*, 2010). The ionomer poly(methyl methacrylate)/cadmium acrylate (PMMA/Cd(AA)₂) was synthesised by free radical polymerization from methyl methacrylate (MMA) and Cd(AA)₂ monomer. The deposition of the ionomer solution under humid condition on to a glass substrate produced ordered porous films. The morphology of the porous films was effectively tuned by changing the concentration of the ionomer solution and the ratio of the monomers. Moreover, CdS nanocrystals were successfully generated in the polymer matrix by exposing the chloroform solution of PMMA/Cd(AA)₂ ionomer to an atmosphere of hydrogen sulphide gas. The evaporation of the solution created BF patterned PMMA/CdS QD-polymer films that exhibits fluorescent properties.

1.9. Properties and Applications of Micropatterned Polymer/Hybrid Films

Super hydrophobic surfaces:

Super hydrophobic materials are very attractive due to their water repellent and self-cleaning properties. These properties are as a consequence of the roughness of the film surface. The combination of hydrophobic polymers and the patterns on their film surface led to a contact angle higher than 150° . These type of pin cushion (figure 1.10) structures can be achieved by peeling off the top layer of patterned film or by chemical/physical surface treatment. Polystyrene containing waxy dendrons are good hydrophobic polymer that can be employed for the preparation of super hydrophobic surfaces by breath figure approach and the patterned films based on these material could achieve a CA of 130° .

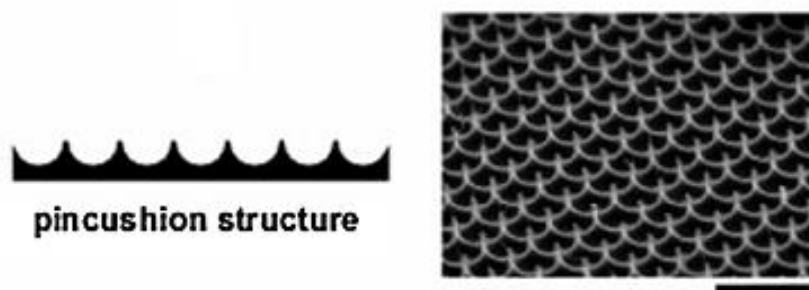


Figure 1.10. Pincushion breath figure patterned flat film

Biomedical Process-cell culturing and adhesion:

Breath figure technique has been considered as a versatile method to fabricate micropatterned cell culture substrate. In addition to the biocompatibility and mechanical strength of the scaffolds, high porosity is also an important factor. The attachment of cells to the substrate is influenced mainly by the depth and size of the pore of the pattern. Different biocompatible and biodegradable polymers

(*Nishikawa et al., 2002*; *Tanaka et al., 2006*) can be employed as a matrix materials and the morphology of the patterns suitable for a particular biological attachment can be regulated by breath figure methods. The cell or biomolecule attachment can be carried out either by casting the solution of an amphiphilic polymer containing ligands which are sensitive towards the attaching substances or a post-modification method can be adopted to introduce the ligand having specific interaction (*Beattie et al., 2006*). Moreover, there are pore specificity for certain type of cell suppressions. Micropatterned surfaces can also be act as an adhesion barriers (*Fukuhira et al., 2008*). Similarly, poly(l-lactic acid) patterned film with Ag nanoparticles can be used with purpose of reducing the bacterial adhesion.

Optical, conductive and magnetic applications:

Breath figure method can be adopted for the fabrication of inverse opals with various pore size and distributions (*Kurono et al., 2002*). The “inverse opals” which are the three dimensional ordered porous structured films with pattern parameters comparable in scale to the wavelength of electromagnetic waves in the visible spectrum, revived great importance in the last decades. Therefore, BF patterned polymer/hybrid films have many potential applications as photonic band gap materials and the photonic behaviour depends on the spatial periodicity of the structure and the refractive index of the materials. The plasmon resonance properties and optical properties of certain inorganic nanoparticles in the hybrid patterned film can be effectively utilized (*Wang et al., 2012*). Moreover, the photocurrent generated in a patterned film surface is higher than that of a flat film surface and hence improved the photovoltaic properties of the organic thin-film

device. The 3D ordered macro-porous structures with conductive polymers and magnetic inorganic compounds leads to electro-magnetic applications.

Templates:

Breath figure patterns can be used as a templates for the patterning of various metal particles and these polymer templates can be removed later on so that a desired microstructures can be fabricated. Metal microstructures can be prepared either by the deposition of metals on a structured polymers or by the direct fabrication of the structured hybrid film in one step by breath figure approach. The deposition of the metal can also be carried out by vapour deposition of metals on the BF polymer film to form hexagonally orders dots (*de Boer et al., 2000*). Another method is the electroplating of the metal on the BF polymer films. The polymer matrix can be thermal decomposed or eluted with a solvent to form the microstructured metal particles. Breath figure method can be utilized to synthesis surfactant-modified SiO₂, TiO₂ and CdS having mesoporous walls by eliminating the organic components by calcination (*Sakatani et al., 2008*). The BF patterned polymer films obtained by breath figure method can also be used as template for pillars or inverse pores by replica molding (*Bolognesi et al., 2005*).

Membranes:

Micropatterned polymer/hybrid films can be employed as membranes for oil/water separation, membranes for fuel cells, micro sieve filtration membranes, etc. Porosity is the important parameter that determines the performance of the membranes to be used as proton-exchange membranes and solid oxide fuel cells. (*Bhadra et al., 2011*). The characteristics for the BF patterned structures to be used as micro sieves involves uniform pore size, a high pore density, and a thickness

smaller than the pore diameter. Moreover, BF films with hierarchical structures provides an integrated supportive structures to enhance the membrane resistance to mechanical stress

1.10. SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Micropatterned polymer films with functionalized breath figure cavities find significant importance due to their characteristics properties for varieties of applications. Post-modification of the liable groups attached to the BF cavities could be a viable route for introducing various functional groups optimized for different applications. Although few works were reported about the functionalized porous polymer film using polymer with terminal or pendent polar groups, self-assembly of functionalized nanoparticles provides a potent way to introduce liable functional groups in the BF cavities. Enhancement of the structural properties is an additional benefit. Hydrophilic as well as hydrophobic particles were used as a BF components. However, they posed certain disadvantages. While the hydrophilic particles reside on the cavity walls and vulnerable to various external forces during applications, the hydrophobic particles reside inside the cavity walls thereby bulk of the desired functionality is not exposed for applications. On the other hand, amphiphilic particles with hydrophilic functional groups are expected to reside inside the cavity walls, but exposing the functional groups at the cavity walls. Amino functionalized BF cavities come into vogue due to their liability towards many reagents by simple chemical reactions. For instances, biomolecules such as proteins, amino acids, carbohydrates, etc. can be covalently bonded on to the breath figure cavities by a condensation reaction between the active amino group of the film and the ester group of the biomolecules. The amino groups present inside the BF

cavities can be converted into the quaternary ammonium salt and negatively charged microspheres are easily trapped inside the holes by gravity and electrostatic interaction because the cavities were enriched with positive charge.

Polystyrene has been used as the matrix material for the present work as it is cheap and more economical. They are chemically inert and being resistant to acids and bases. Several studies were reported about the BF formation with polystyrene in the form of star-homopolymer and linear polystyrene with or without polar terminal groups under various experimental conditions and each of these works claimed the presence of a polar group to promote the stabilization of breath figure patterns. Here, we used commercially available atactic polystyrene which does not form BFs under our experimental conditions but forms regular array of BF concavities in the presence of the amphiphilic-modified alumina particles. Therefore, it is worthwhile to explore the possibility of synthesising and using amphiphilic particles with amino group as the hydrophilic component to produce BF patterned polystyrene film with amino functionalised cavities.

Hence, the main objectives of the present investigation are:

- i) To synthesize and characterize amino-functionalised amphiphilic alumina nanoparticles for application in particle-assisted formation of micropatterned films by drop-casting method.
- ii) To investigate the factors controlling the formation and the morphology of micropatterned polystyrene-alumina hybrid films with amino-functionalised breath figure cavities.
- ii) To explore the possibility of fabricating free-standing micropatterned films and for tuning the pore morphology.