

Droplet condensation on polymer surfaces: a review

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Abstract: Dropwise condensation on substrates is an important topic of interest because it plays a crucial role in many scientific applications such as heat transfer, water harvesting from the humid atmosphere, and polymer templating. We focused on droplet condensation on polymer surfaces and briefly summarized the drop condensation studies reported in the last 2 decades and their potential applications. The main topics discussed in this review are water harvesting from dew using radiative cooling; using surfaces synthesized by bio-inspiration; experimental, theoretical, and simulation studies on the growth of breath figures; drop condensation on superhydrophobic surfaces and on self-assembled monolayers; and hexagonal pattern formation on polymers using the breath figures method. This review does not cover dropwise condensation studies in heat transfer phenomena since polymers are rarely used for this purpose due to their low heat transfer coefficients.

Key words: Drop condensation, breath figures, water harvesting, superhydrophobic, bioinspired surfaces, polymer templating

1. Introduction

A phase change occurs by condensation from the vapor state to the liquid state when the vapor temperature is below the saturation temperature corresponding to its pressure, or alternatively vapor condenses on a solid surface whose temperature is below the saturation temperature of the vapor. The latter, surface condensation, is classified into 2 groups as dropwise or filmwise condensation. On practical surfaces, one or both of these can occur depending upon the wetting characteristics of the condensing surface. A liquid film forms in filmwise condensation that is resistant to heat transfer, whereas dropwise condensation occurs on a surface that is not completely wetted by the liquid condensate, and the surface is covered by droplets whose size ranges from a few micrometers to millimeters and that are visible to the naked eye. In addition, the resistance on heat transfer greatly decreases due to the absence of a continuous film on the condensing surface, which makes dropwise condensation an attractive mechanism for industrial heat transfer applications.^{1,2} Besides its advantages on the heat transfer phenomenon, dropwise condensation has been used for water harvesting from the humid atmosphere by using bio-inspired, superhydrophobic surfaces. Recently, ordered pattern formation methods on polymer surfaces have been successfully developed using the breath figures formed by drop condensation.

In this review, we focused on droplet condensation on polymer surfaces. The selected topics are divided in the 5 groups: water harvesting from dew using radiative cooling, or on surfaces obtained by bio-inspiration; experimental, theoretical, and simulation studies on growth of breath figures; dropwise condensation on superhydrophobic surfaces; and dropwise condensation on self-assembly monolayers and pattern formation on polymers

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Dedicated to the memory of Professor Ayhan S. Demir

using breath figures. We do not include the applications of dropwise condensation in heat transfer in this review since polymer-coated metals are rarely used for this purpose due to their low heat transfer coefficients.

2. Water harvesting

2.1. Water harvesting from dew using radiative cooling

Dew is a potable water source for plants and small animals in the case of small water requirements in arid and semiarid areas.³ Many researchers have been inspired by this process to produce fresh water from the atmosphere. Specially built dew condensers were established to increase the yield of dew water by radiative cooling.^{4–29} Although large quantities of water cannot be provided, dew water collection may be very important when small quantities of water are needed in warm countries, especially for military purposes.

Nilsson carried out the initial outdoor dew collection experiments in Sweden and Tanzania by using radiatively cooled pigmented LDPE foils. Condensation occurred when the temperature of the water vapor became lower than the dew point temperature. They observed that in arid places water is condensed in the few last hours before sunrise. The main restriction for large condensed water volumes was the low humidity during most of the nights.⁴

Vargas et al. carried out radiative cooling dew collection experiments in Tanzania in 1998 using low density polyethylene (LDPE) foil with a thickness of 390 μm and pigmented with 5 vol% TiO_2 and 2 vol% BaSO_4 . The surface area of this foil was 1.44 m^2 with a 20° tilt angle from the morning sun and 1.43 L/m^2 dew was collected as monthly average.⁵ Pollet and Pieters quantified the radiation transmittances of an ordinary LDPE film and a standard glass plate in a period of complete condensation for the angles of 0, 30, and 60°. The cladding materials showed a transmission decrease in dry conditions with the increase of incidence angles. The authors concluded that the effects of condensation on the radiation transmittance were greater on the LDPE film than on the glass plate.⁶ In a further work, Pollet and Pieters examined the transmittances of single glass, low-emissivity glass, double glass, LDPE, anti-drop-condensation polyethylene, and anti-dust polyethylene for dry and wet situations under laboratory conditions. Experimental results showed that the shapes of the condensate drops were much smoother on glass than that on non-anti-drop plastics. Lower transmittance values were obtained for glass surfaces than plastics because of the uniform diffusion of radiation.⁷ Pollet et al. examined the diffusive properties of glass, LDPE, and anti-drop condensation polyethylene (ADCPE) under dry and condensate covered conditions and found that plastic materials diffused more transmitted radiation than glass, which behaves as a quasi-non-diffusive material in dry conditions. All the materials showed an enhanced transmitted radiation (except ADCPE) when covered with the condensate.⁸

Beysens and coworkers reported many experimental findings in this field. They described the main physical principles of the functionality of dew condensers and they suggested a model to simulate them in 1996. They showed that the ideal condenser is a 'grass-like' light sheet thermally isolated. They reported that approx. 1 L m^{-2} condensed water should be yielded when a sheet of polyethylene is used by assuming that there is no evaporation and that all the condensed water flows into a vessel.⁹ Beysens and coworkers investigated the optimal conditions for dew production from the atmosphere with a condenser that was installed in Grenoble, France. They determined that an angle of 30° with respect to horizontal is the optimal condition for dew production because of the weak wind influence, large light-emission solid angle, and easy drop collection by using TiO_2 and BaSO_4 microspheres embedded LDPE sheets.¹⁰ Beysens and coworkers produced a well-designed inexpensive radiative condenser made of TiO_2 and BaSO_4 microspheres embedded in LDPE. The rectangular condensing surface had a tilt angle of 30° and it was set up in Corsica, France. A horizontal

polymethylmethacrylate (PMMA, Plexiglas) reference plate was also used in the dew collection measurements for comparison. 3.6 L/day average yield was obtained and chemical analysis showed that the harvested dew water was potable in spite of the weakly acidic pH and high suspended solid concentration.¹¹ In a further study, the authors installed 2 large dew condensers in Corsica, France with a tilt angle of 30° and the collected water amounts were compared to reference plates that were made of PMMA and polytetrafluoroethylene (PTFE). The amount of dew water was increased for both of the prototypes when compared with the horizontal reference plates. An obviously larger yield was obtained for the exposed condenser than for the ground condenser. The reason was associated with scattering solid angle, which protects from the heating effect of the environment.¹² Beysens and coworkers conducted chemical and biological analyses to test the quality of dew water and found that it should be purified due to the fact that the collected water is contaminated with microorganisms and bacteria.¹³ Another experiment was carried out in Bordeaux, France, over 1 full year, using TiO₂ and BaSO₄ microspheres embedded in LDPE with a 1 vol% of a surfactant additive nonsoluble in water. They reported that the chemistry of dew water and rainwater looks similar and for potable water they found that the average ion concentrations are below the World Health Organization (WHO) limit values.¹⁴ In a further work, Beysens and coworkers investigated the relative contributions of dew and rainwater at the Mediterranean Dalmatian coast and islands of Croatia using condensers made of TiO₂ and BaSO₄ microspheres embedded in a LDPE matrix that also contains an insoluble surfactant additive on its surface, and they concluded that a sufficient amount of water could be obtained as a supplementary water source by dew collection studies even if the measurements were conducted during the dry season.¹⁵

Muselli reported the effect of color of inexpensive painted coatings and found that white painted materials permit a decrease in air-conditioning electrical energy by 26% to 49% according to the roof cover composition.¹⁶ Meanwhile, Maestre-Valero et al. analyzed the dew collection capacity of 2 different high-emissivity LDPE foils: a white hydrophilic foil and a low-cost black foil. Experiments were conducted in southern Spain in a semi-arid area over a 1-year period. They reported that black LDPE foils show more spectral emissivity than white hydrophilic LDPE foils. Because of its hydrophilic properties, white hydrophilic LDPE foil was more sensitive for the formation of dew than the black PE foil. However, the annual cumulative dew yield for black foil was higher than for white foil due to its higher emissivity and emitted radiance properties.¹⁷ In a further study, Maestre-Valero et al. estimated the dew yield using an energy balance modeling approach to predict the nightly water yield of 2 passive radiative dew condensers tilted 30° from the horizontal in southeastern Spain. The results showed that the simulated dew yield was highly sensitive to changes in relative humidity and downward longwave radiation.¹⁸

In a further study, Beysens and coworkers investigated the effect of the local parameters (e.g., wind speed, humidity) on the general properties such as seasonal variation of night duration by using a horizontal PMMA reference plate and compared dew data obtained from 3 different sites: a continental coastal Atlantic area (Bordeaux, France), a continental alpine valley (Grenoble, France), and a Mediterranean island (Corsica, France) during the long period of approximately 4 years. It was found that heat and mass transfer coefficients can be varied and these 2 parameters are identical for the 2 continental sites.¹⁹ Beysens and coworkers used TiO₂ and BaSO₄ microspheres embedded in LDPE foil-based radiative condensers and chemical and biological analyses showed that the collected water was potable and a significant amount of fresh water can be obtained by using inexpensive passive radiative dew condensers.²⁰ They also studied polycarbonate commercial plastic as house roofing material for its advantages on higher dew collection ability and easier installation and obtained a 26% increase in the total collected water.²¹ Beysens and coworkers collected a full year of dew, fog, and

rain in the dryland area of Mirleft, Morocco, for an alternative water source. For this purpose, they used 4 passive dew condensers and a passive fog net collector all with 1 m² surfaces. They used TiO₂ and BaSO₄ microspheres embedded LDPE condensing foil with an insoluble surfactant additive on its surface to enhance dewdrop flow. From the chemical and biological analysis, they obtained ion concentrations compatible with World Health Organization (WHO) recommendations. On the other hand, harmless vegetal spores and little contamination by animal/human bacteria were obtained from the biological analysis.²²

Cemek and Demir designed 8 model pitched roof greenhouses in Samsun, Turkey, to measure light transmission of plastic films in wet and dry conditions. They used UV stabilized polyethylene (UV-PE), IR absorber polyethylene (IR-PE), LDPE with no additives, and double layer polyethylene films (D-LDPE) as substrates and the results show that light transmission under dry conditions was higher than that under wet conditions for all kind of plastics. D-LDPE showed the lowest light transmission while LDPE showed the highest. It was also concluded that an increase in condensation area results in a reduction in the light transmission of covering plastics.²³ Gandhidasan and Abualhamayel offered a renewable method for harvesting fresh water as dew from the atmosphere by using TiO₂ and BaSO₄ microspheres embedded LDPE foil with a thickness of 350 μm in Dhahran, Saudi Arabia, and 0.22 L/m² water was yielded. Experimental results were compared with a formulated steady-state mathematical model and a good agreement was obtained between them. It was found that collected dew amount increased with an increase in wind speed.²⁴ Clus et al. collected dew on a Teflon foil coated collector for the purpose of thermal insulation with a 30° tilt angle to show that potable water could be obtained for a rainless area such as in the Pacific islands of French Polynesia.²⁵ Jacobs et al. performed dew collection experiments in the center of the Netherlands over a period of 18 months with 2 types of specially designed dew collectors: an inclined planar 0.39 mm LDPE collector with 30° tilt angle and an inverted pyramid-shaped collector.²⁶ The inverted pyramid-shaped collector was built to reduce the view angle to only the nighttime sky; however, it was found that the collected water difference between them was only 5%. They concluded that surface drainage plays a dominant role in dew collecting and is usually underestimated.²⁶ Clus et al. built 3 pilot condensers as terrace, roof, and ground type made of 2 layers of polyethylene shading net, in a village in southern Morocco, and collected data for 6 months. Water production was more than 0.2 m³/day.²⁷

Sharan et al. installed the biggest (850 m² total surface area) dew and rain collecting system in the semi-arid area of Kutch, India. Chemical and biological analyses proved that the collected water is potable if it is filtered and treated with light to increase its pH.²⁸ Lekouch et al. analyzed collected dew and rain water in Zadar, Croatia, using a 0.35-mm thick LDPE condensing foil (TiO₂ and BaSO₄ microspheres embedded and with a food surfactant) over a period of 3 years. Mean pH of dew and rain was slightly acidic (6.7 and 6.35). Both dew and rain water generally were sufficient in terms of WHO requirements for potable water, except for Mg²⁺, whose concentration was about 6 times larger than the maximum recommended value (0.5 mg L⁻¹).²⁹

2.2. Water harvesting surfaces by bio-inspiration

The Stenocara beetle, which lives in the Namib desert, can obtain its potable water by condensing water vapor on its back.^{30–34} The structure of the Stenocara beetle's back consists of hydrophilic bumps used to facilitate drop condensation and channels having a superhydrophobic overlayer that serves as a guide for the accumulation of water droplets to flow directly down to the beetle's mouth from fog-laden wind. Some researchers have mimicked the beetle's back to fabricate surfaces with special wettability.^{31,35–39}

Parker and Lawrence mimicked the skin of the *Stenocara* beetle by generating hydrophilic bumps on superhydrophobic films with the help of the ordered arrays of 0.6-mm glass spheres on a waxy background. They concluded that ordering hydrophilic points on the hydrophobic parts was the best design to collect water from the mist and proposed that this inexpensive fog-collecting structure can be projected to the commercial scale by injection molding or printing techniques.³¹ Zhai et al. produced a surface structure using a polyelectrolyte as hydrophilic patterns on superhydrophobic surfaces to mimic the *Stenocara* beetle's back. Polyallylamine hydrochloride (PAH)/polyacrylic acid (PAA) substrates with PAH/silica nanoparticles were impregnated in a network of semi-fluorosilane for the fabrication of the superhydrophobic surface and arrays of hydrophilic spots were generated on the substrate by adding drops of a solution of polyacrylic acid (PAA) in H₂O/2-propanol with a micropipette. Similar to the *Stenocara* structure, condensed droplets on the hydrophobic spots grow with coalescence and give bigger drops, whereas no wetting was observed on the superhydrophobic background.³⁵ Garrod et al. also obtained a plasma chemical patterned superhydrophobic–superhydrophilic surface to mimic the *Stenocara* beetle's back. The superhydrophobic background was fabricated by CF₄ plasma-fluorinated polybutadiene and O₂ plasma etched poly(tetrafluoroethylene) while poly(4-vinyl pyridine) was used for the creation of superhydrophilic spots. They compared water microcondensation performances of this surface design to the surface present on the *Stenocara* beetle's back and compatible results were obtained.³⁶

Dorer and Ruhe developed superhydrophobic surfaces patterned with circular hydrophilic patches and circular hydrophilic bumps were generated by dispensing defined volumes of poly(dimethylacrylamide), poly(heptadecafluorodecylacrylate), and poly(styrene) polymer solutions onto nanoglass surfaces using a pipette. After exposing these surfaces to the foggy atmosphere, condensed drops on the hydrophilic patches reach a critical volume and roll down with the effect of gravity. They investigated the critical volumes to enable rolling of the droplets from the substrates at a specific range of wetting contrasts, patch diameters, and tilting angles. The pinning effect was also examined in this study and the results showed that the pinning force is constant and independent of the drop volume for a given bump.³⁷ Ke et al. prepared a superhydrophobic n-octadecylsilane (PODS) surface that had a 159° water contact angle and 0° sliding angle. Hydrophilic regions on the superhydrophobic surface were obtained by anchoring SiO₂ nanoparticles on to the PODS surface. The SiO₂/PODS surface exhibited superior dew ability similar to that of the back surface of the *Stenocara* beetle.³⁸ Thickett et al. synthesized a biomimetic micro-patterned surface with hydrophilic bumps on a hydrophobic background as on the *Stenocara* beetle's back. These surfaces consisted of a series of isolated droplets and interconnected cylinders of poly(4-vinylpyridine) on a PS background.³⁹

On the other hand, water droplets condense on the spider's web by hanging especially in the early morning and the combination of the surface energy and curvature gradients provides driving ability to the silk for the condensed droplets directionally from the “joints” to the “spindle-knots”. Some researchers have been inspired by spider silk for water collection using the humidity sensitive structure and outstanding mechanical properties.^{40–46} Zheng et al. prepared an artificial spider silk by immersing uniform nylon fiber into poly(methylmethacrylate)/N,N-dimethylformamide–ethanol solution and then horizontally drawing out quickly. The thin polymer film formed on the fiber broke up into a series of tiny solution drops. After drying of these droplets, periodic spindle-knots formed, similar to those of spider silk. In their study, Zheng and coworkers also prepared a surfactant modified spider silk by using a dilute sodium dodecyl sulfate (SDS) surfactant solution and showed that their artificial spider silk has a water collection ability similar to that of natural spider silk.⁴⁰ Bai et al. fabricated a series of bioinspired artificial spider silks by immersing a uniform nylon fiber into PMMA solution in DMF and drew out it horizontally using a dip-coater. PMMA film breaks up into polymer droplets

owing to the Rayleigh instability on to the fiber and periodic PMMA spindle-knots on the nylon fibers form artificial spider silks after the evaporation of the solvent. They showed that their artificial silk could be applied for collecting water from fog.⁴¹ Lei Jiang and coworkers developed a fluid-coating method for the fabrication of periodic spindle-knotted bioinspired fibers by using PMMA in DMF as polymer solution. They drew out the nylon fiber into the polymer solution, then the film broke up into droplets owing to the Rayleigh instability after coating, and periodic spindle-knots were formed. Numerous tiny water droplets generated by an ultrasonic humidifier condensed on this bioinspired fiber. Results showed that bioinspired fiber is capable of directional water collection with the cooperation of Laplace pressure gradient from the curvature difference of the spindle-knot shape and the surface energy gradient formed from the difference in surface roughness.⁴²

In a further work, Jiang and coworkers used polyvinylidene fluoride (PVDF) instead of PMMA to fabricate a bioinspired spindle-knotted fiber. Multi-level spindle-knots that supply continuous gradients of surface energy and different Laplace pressures are formed after the drying process with phase separation. Under humid conditions, they observed the collected water far greater than for a normal uniform fiber as a result of the size effect of the spindle-knot, which is associated with the capillary adhesion of hanging drops.⁴³ Jiang and coworkers also produced knotted fibers on a large scale using coaxial electrospinning. For this purpose, PS solution was used as inner solution and a dilute PMMA solution was used as outer solution. They stretched the inner PS solution for the formation of fibers and flowed out the outer PMMA solution with the inner solution to adhere on the surface of PS fiber. Just after the complete evaporation of the solvent, knotted microfiber was obtained. When this fiber was exposed to a foggy atmosphere, condensation occurred as tiny water droplets on this fiber and water droplets moved toward the knots by integrating with each other instead of evaporating again at their initial location. They reported that since the fiber serves as a water collecting system, this method could be considered a promising way for rapid, large area, and inexpensive water collection applications.⁴⁴ Jiang and coworkers used carbon fiber instead of nylon in a further work to obtain knotted bioinspired fibers. They immersed carbon fiber specimens into PVDF–DMF solution with a 200 mm s^{-1} draw out rate horizontally to form a fiber network similar to the geometric structure on the wetted spider silk. Then they solidified an epoxy resin to coat this network. Results showed that this special bioinspired fiber had higher water collecting efficiency.⁴⁵ Jiang and coworkers also examined the effect of geometry on the hanging-drop ability and found that the geometry of bioinspired fiber presents a much stronger water-hanging ability when compared to the uniform fiber. With the control of the movement of tiny water drops, geometry enhances the fog collection ability.⁴⁶

3. Growth of condensed droplets

Breath figures are tiny droplets that form when the vapor present in the atmosphere condenses on a cold surface,^{47–67} and they have been used as an effective way for the detection of the cleanliness and uniformity of glass surfaces for a long time.⁴⁷ In the condensation process, breath figures and the surface properties of the condensing substrate play a vital role. In the case of dropwise condensation, numerous minute droplets are initially formed after the vapor impinges on a surface cooled at a temperature below the saturation temperature, releasing the latent heat of condensation. These droplets start to grow rapidly due to the continuing direct condensation of vapor onto them by diffusion following the same kinetics as with drop evaporation.^{68–82} Meanwhile, some droplets touch each other and coalesce to create larger drops and droplets shift from their positions a little at each coalescence, leaving open areas behind them on the surface where initial droplets can be nucleated to start the recycling process again. Beysens reviewed the heterogeneous nucleation and growth

of condensed water droplets with a discussion on the heterogeneity of the substrate and the effect of gravity. He reported the importance of the temperature and wetting properties of the substrate on the control of the nucleation rate and the major consequences on the form and growth of the droplet pattern.⁴⁸

The number of condensed droplet per unit area and mean droplet sizes also vary according to the solid surface properties. In many experimental studies, water vapor at a specific humidity was sent onto cool surfaces resulting in rapid condensation.^{49–51,53,58,61,62,65} On the other hand, condensation of water vapor from ambient air (without sending vapor to cool surfaces) was also studied.^{59,63,64} Many studies also investigated the growth dynamics of condensed droplets applying theoretical models and simulation.^{83–99}

3.1. Experimental and modeling studies on growth of breath figures

Beysens and Knobler investigated the condensation of water vapor on a vertical octadecyltrichloro silanized glass surface. They determined that at a 0° contact angle a uniform liquid layer forms whose thickness grows as t at constant ΔT . However, at a 90° contact angle of drop on a surface occupied with droplets at constant ΔT , isolated condensed droplets grow according to $t^{0.23}$ while the average droplet radius grows as $t^{0.75}$ in the case of coalescence existing between the droplets.⁴⁹ In a further study, Beysens and coworkers studied the growth of droplets on the same surface to examine the importance and the effects of the carrier-gas flow velocity, the nature of the gas, the experimental geometry, and heat transfer through the substrate. A “1/3” exponent of time was reported for the growth of individual drops. The effect of substrate temperature on the drop condensation rate was explained by the fact that an increase in substrate temperature at high flow velocities results in a decrease in the drop condensation rate and gives lower growth law exponents. In the case of coalescence between the droplets, the condensation rate accelerates. They also compared their experimental results with the predictions of scaling laws and simulations.⁵⁰ Zhao and Beysens carried out heterogeneous drop condensation experiments on decyltrichlorosilane silanized silicon wafers to produce a wettability gradient on substrates from hydrophobic to hydrophilic side where contact angle displayed a continuous change from beyond 90° to a few degrees. It was found that the contact-line-pinning on the chemically heterogeneous surface prevented the full coalescence of droplets, and the saturated surface coverage is significantly increased depending on the contact angle hysteresis (CAH) strength.⁵³

In a further study, Beysens and coworkers examined the coalescence dynamics of 2 water sessile drops and compared it with the dynamics of spreading of a single drop on silicon wafers and polyethylene surfaces. After coalescence, the newly formed drop relaxes for equilibrium with decreasing contact angle and the time for relaxing varies depending on the initial conditions and the surface properties of the substrate. Results showed that the dynamics of coalescence between the contacting droplets is systematically faster by an order of magnitude when comparing with the coalescence by the help of syringe deposition. They observed that the drop is actively excited by deformation just after syringe deposition, favoring contact line motion.⁵⁴ Narhe et al. investigated the dynamics of drop coalescence of 2 water drops on a silicon wafer and polyethylene surface and the results were compared with drop spreading. They concluded that drop coalescence dynamics and drop spreading motion were in the same order if coalescence or spreading was induced by a syringe. Dynamic analysis results showed that condensation-induced coalescence was slower than the coalescence induced by syringe deposition and this situation was attributed to the coupling of the contact line motion with the oscillation of the drop in conditions of syringe deposition but this is not present for condensation-induced coalescence.⁵⁶ Beysens reported that temperature and the wetting properties of the substrate not only control the nucleation rate, but also have major effects on the form and growth of the droplet pattern. Surface treatments can be applied for the modification of the wetting properties of substrates.⁵⁸

Meanwhile, Briscoe and Galvin reported an experimental study on the condensation of water vapor on a flat polyethylene film where CAH is negligible. They proposed that condensed droplets can grow with 2 different growth laws. In the first regime of condensation, droplets behave as isolated and coalescence between droplets has a negligible effect on the average rate of droplet growth. In this stage, growth of droplets was limited by the rate at which latent heat could be dissipated. In the second regime, coalescence had its maximum effect on droplet growth and latent heat was easily dissipated between the droplets. Briscoe and Galvin also showed that the mean diameter of the droplets scaled as $[D \propto \text{time}^{1/3}]$ during the first regime and scaled as $[D \propto \text{time}]$ for the second regime. Their results were in good agreement with the semi-empirical equation proposed by Vincent⁵² and derived by Briscoe and Galvin, which describes the evolution dependence of the fraction of droplet coverage over number of droplets per unit of substrate area, which is independent of the nature of the intrinsic growth.⁵¹ Briscoe et al. investigated water vapor condensation on polyethylene and corona discharge treated polyethylene films to examine their effectiveness and durabilities. Corona discharge treatment on polyethylene introduced hydrophilic groups on the surface and caused a distortion of the drop geometry. Hydrosol particles were applied to polyethylene film surfaces for the purpose of improving wetting properties. Both of the surface treatments showed significant degradations over time.⁵⁵

Lauri et al. presented theoretical and experimental studies on heterogeneous nucleation and condensation of water vapor onto 3 different surfaces (newsprint paper, Teflon, cellulose film) to investigate phase transitions and mass fluxes of supersaturated water vapor on these substrates. Their results show that smaller onset supersaturations and smaller experimental condensation growth rates were obtained than the modeled ones with time.⁵⁷ Leach et al. studied dropwise condensation of water vapor on a commercial grade polyvinylidene chloride (PVDC) film and glass slides treated with octadecyltrichlorosilane for comparison to investigate nucleation and growth. It was concluded that the smallest drops grow mainly by the diffusion of water vapor while drops of diameter larger than 50 μm grow principally by direct deposition from the vapor onto the drop surface. The drop size distribution was determined mainly with the coalescence step. They obtained good agreement between simulation and experimental results. Condensation rates per unit substrate area for small drops were much higher than those for areas occupied by large drops.⁵⁹ Song et al. assumed that steam molecules make clusters before condensation on a cooled surface and investigated the condensation of moist air on surfaces having different wettabilities using a high speed camera and microscope. They claimed that droplet size distributions were consistent with the presented cluster theory for both hydrophobic and hydrophilic surfaces.⁶⁰

Sokuler et al. investigated nucleation and growth of condensing water droplets on 0.3-mm thick films of poly(dimethyl siloxane) (PDMS) with varying cross-linking density as soft polymeric substrates and they showed that condensation on soft surfaces leads to different patterns than those on hard surfaces. An increase in nucleation density was obtained with an increase in the softness of the substrates. An increase in softness also caused longer relaxation times for drop shape equilibrium after coalescence of 2 droplets and prevention of merging on very soft substrates. Higher surface coverage values and higher condensed drop volumes were obtained on soft surfaces by means of all of these effects.⁶¹ In a further study, Sokuler et al. applied diffusion based evaporation equations for a condensing drop.⁶² They conducted water drop condensation experiments on a very small silanized AFM cantilever that limits the maximum width of the growing droplets. They showed that dropwise condensation and evaporation follow the same kinetics and they applied drop evaporation equations for the drop condensation process since both drop evaporation^{68–82} and condensation are diffusion limited. In a dense array of drops, each individual drop grows steadily and linearly with time, $V \propto t$, while the volume of single isolated droplets changes according to $V \propto t^{3/2}$. The growth rate of the condensed droplets is associated

with the amount of excess water vapor in the air and in the case of many droplets lying on a plane close together all of them grow steadily over time regardless of their size since each distorts the vapor distribution near its neighbors, effectively smoothing out the distribution across the plane. However, for an isolated droplet, the vapor distribution conforms to the dome-shaped single droplet, and the amount of vapor condensing into it at any moment increases with its radius.⁶²

Ucar and Erbil found that diffusion based drop evaporation equations^{68–82} can be used successfully to estimate the rate of drop growth of a single droplet that condensed on PP, HDPE, PPPE, LDPE, and EVA polymer surfaces just below the dew point temperature.⁶³ It was determined that the condensation rate of a single isolated droplet decreased with an increase in surface roughness and corresponding initial contact angle and contact angle hysteresis. They found that the drop radius of the individual isolated droplets grows according to a power law with exponent 1/3 except for PP surface similar to previous reports.^{48–51,58} Growth rate of a single droplet surrounded by other droplets was found 14%–40% lower than that of a single isolated droplet because of the barrier effect to lateral vapor diffusion.⁶³ In a further study, Ucar and Erbil investigated the dropwise condensation rate of water breath figures on polyolefin polymer surfaces whose surface free energies were in a close range of 30–37 mJ/m² but having different surface roughness and *CAH*.⁶⁴ They studied in ambient conditions at a temperature just below the dew point and it was determined that an increase in surface roughness and corresponding initial contact angle and *CAH* of polyolefin polymer surfaces results in an increase in the initial number of condensed droplets per unit area during the nucleation stage. In addition, the total volume of condensed water (growth rate of water droplets) and surface coverage for the growth stage by diffusion increased with surface roughness. Moreover, it was confirmed that mean drop diameter of condensed droplets on these polymer surfaces grows according to a power law with exponent (1/3) of time.⁶⁴

Sikarwar et al. observed dropwise condensation on a chemically textured silanized glass surface and investigated the effects of the contact angle, *CAH*, tilt angle of the substrate, thermophysical properties of the working fluid, and the saturation temperature of condensation.⁶⁵ Model simulation results were compared with the experimental data and it was found that an increase in static contact angle and tilt angle resulted in a decrease in the surface coverage of the droplets. High tilt angles resulted in a larger number of small drops and higher heat transfer coefficient.⁶⁵ Anand and Son used a subcooled silicon surface with a static contact angle of 60° as the condensation surface and superheated vapor having low pressures of 4–5 Torr was condensed on it. This process was monitored by ESEM microscopy and the results showed that droplet growth is a function of time and growth rate decreases with the increase in droplet size.⁶⁶

Yu et al. examined the deposition of fog on smooth and square pillar textured silicon substrates after coating with a hydrophobic fluoroalkylsilane monolayer. For smooth substrates, they observed a similar deposition process with condensation. However, they stated that differences in length scale revealed a transient regime not reported in condensation experiments. For pillar textured substrates, when the mean drop size was smaller than the pillar an enhancement in drop coalescence was obtained. On the other hand, inhibition was observed on the coalescence when the drops were comparable to the pillar size.⁶⁷

3.2. Theory and simulation studies on growth of breath figures

Rose and Glicksman presented a universal form of the distribution function for large drops, which grow primarily by coalescence with smaller drops, though smaller drops themselves mainly grow by direct condensation to find an asymptotic surface coverage as 0.55 and concluded that the third stage of dropwise condensation could be defined as a droplet growth and coalescence model.⁸³ Viovy et al. investigated continuous growth and

coalescence with neighboring droplets theoretically.⁸⁴ They developed a theory for 3D objects on 2D substrates and reported that the growth exponent of a single droplet should be $1/3$, while the growth exponent of a mean droplet should be unity. Experimental comparisons were also performed.⁸⁴ Familiy and Meakin developed a simple droplet growth model and showed that asymptotic droplet size distribution has a bimodal structure and has good agreement with the experiments.⁸⁵ Fritter et al. investigated the growth of breath figures by computer simulations. They presumed a power law for the individual droplets and they found that average radius of droplets, droplet distribution sizes, surface coverage, and radial distribution function were a function of time and were in good agreement with the experimental results.⁸⁶ By using a mean-field boundary layer approximation, Rogers et al. developed a model of diffusion limited droplet growth and showed that individual droplets grow with $1/4$ exponent of time.⁸⁷

Briscoe and Galvin described an analytical model for evaluation of the growth of breath figures predicting that intrinsic growth of the droplets follows a simple scaling law. This model also predicts the mean diameter of the droplets, surface coverage, and the number of droplets per unit area, as functions of time from the onset of condensation where the effect is small, up to and including the intermediate, self-similar regime.⁸⁸ In a further study, Briscoe and Galvin used Vincent's equation⁵² to obtain a simple analytical solution to fit their simulation results. They showed the time dependence of area-based mean diameter of the droplets, the fraction of the surface coverage, and the number of the droplets per unit area, and presented general descriptors for the growth of breath figures.^{89,90} Derrida et al. considered a monodisperse droplet size distribution and using the mean-field approximation they showed that the distribution of the distances between neighboring droplets obeys a Smoluchowski equation, which was solved analytically to determine coverage and the distribution distance between the droplets.⁹¹ Steyer et al. explained that a motionless droplet that grows with diffusion can be shown to asymptotically grow as $t^{1/3}$; however, they reported that the growth law exponent is very sensitive to the boundary conditions.⁹² Meakin simulated all 4 stages of dropwise condensation (nucleation and growth; growth and coalescence; growth and coalescence with renucleation in exposed regions; and growth, coalescence, and renucleation with removal of larger droplets) using simple computer models and reported that the results of these models can be described in terms of simple scaling theories.⁹³ Abu-Orabi used the population balance concept to predict the distribution of the size of small drops on surfaces where condensation takes place by small drops that grow by direct condensation. Using the drop size distributions and the rate of heat transfer through a single drop, they calculated the total heat flux.⁹⁴ Burnside and Hadi simulated dropwise condensation of steam where they chose the time steps to be the intervals between successive coalescences anywhere on the surface and reached up to $4\text{-}\mu\text{m}$ drop size as the maximum value and compared their results with the literature values.⁹⁵

McCoy developed a theory by applying a population balance equation based on cluster distribution kinetics for single-monomer addition and dissociation. Droplet growth was explained by combining cluster dynamics.⁹⁶ Wu et al. simulated drop size and spatial distributions with high precision by using the random fractal model and their numerical simulation results were in good agreement with the bulk of existing experimental data.⁹⁷ Ulrich et al. simulated the homogeneous deposition of liquid droplets having a 90° contact angle on a smooth and chemically homogeneous flat substrate and reported that no matter what the contact angle is the surface coverage always saturates at the value after some time, while the dynamics of homogeneous deposition is strongly affected by the contact angle.⁹⁸ Mei et al. simulated the nucleation, growth, renucleation, and sweeping steps of the drop condensation process based on the intrinsic growth rate of a single droplet and concluded that initial number of droplets highly affected the growth rate of the droplets.⁹⁹

4. Dropwise condensation on superhydrophobic surfaces

It is necessary to remove large condensate drops from the condensing surface to provide a continuous water supply, especially at the last stage of drop condensation, and superhydrophobic surfaces appear to be an ideal solution to this problem.^{100–102} Superhydrophobic surfaces are rough surfaces having water contact angles larger than 150° and water drops fall off with a very small tilt angle.^{103–105} There are air pockets around the protrusions on the surface and the water drop sits on both the air and solid layer where the water/solid contact area is much smaller than the water/air contact area. Water drops easily roll off from a superhydrophobic surface even if only very small forces are applied, e.g., giving a slight tilting angle to the substrate. Hence, rolling drops leave the surface completely dry and clean. Due to these self-cleaning and other useful properties, superhydrophobic surfaces became the focus of scientific and technological interest.^{103–130} The mechanism of very large contact angle formation on superhydrophobic surfaces has been recently investigated^{106,107} and the application of the well-known Wenzel¹⁰⁸ and Cassie–Baxter¹⁰⁹ equations was discussed.

On the other hand, drop condensation on superhydrophobic surfaces has become one of the rapidly expanding topics in surface science.^{110–130} Lau et al. conducted vapor condensation experiments on a superhydrophobic surface obtained by vertically aligned carbon nanotubes having nanoscale roughness coated with a poly(tetrafluoroethylene) coating in 2003 and showed that both nanotube forest and the low surface energy coatings were necessary components.¹¹⁰ Narhe and Beysens studied the growth dynamics of condensed water drops on a geometrically patterned superhydrophobic surface where decyltrichlorosilane coated patterned silicon substrates were used.¹¹¹ Air pocket superhydrophobicity was not observed on grooved substrates during drop condensation.¹¹¹

In a further study, Narhe and Beysens showed that if the drop radius on the top surface reaches the cavity size, 2 probable situations may exist: (i) the drop can coalesce with the other drops present in the cavity and get sucked in, resulting in spectacular self-drying of the top surface and/or (ii) coalesce with another drop on the top surface, resulting in a drop on air pockets.¹¹² The authors characterized the initial stage of condensation by nucleation of the drops at the bottom (cavities) of the spikes. In the intermediate stage, small drops within the neighboring cavities surround the large drops described as a “bright ring” that remain until the coalescence occurs with the central drop.¹¹² Narhe and Beysens also examined the growth dynamics of condensed water drops on a model rough hydrophobic square pillar silicon substrate that were silanized with decyltrichlorosilane.¹¹³ They reported that similar growth laws were valid with the drop condensation on flat surfaces; however, transition to an air-pocket-like state occurred due to the bridging of the drops between the pillars. Later, transition to a more stable sucked state occurred by a pillar self-drying process. In the very last stages of dropwise condensation, they observed that a few large drops were fed by neighboring channels.¹¹³

Wier and McCarthy reported that water droplets nucleated and grew both on top of and between the pillars on an ultrahydrophobic surface and when drop condensation progressed condensed water between the pillars was forced upward to the surface. Condensed droplets were pinned at the contact lines and water drop mobility decreased on the patterned surfaces.¹¹⁴ Dorer and Ruhe conducted drop condensation studies on fluoropolymer coated microstructured silicon post surfaces.¹¹⁵ They reported that, in the case of microscopic droplets, they are only in contact with 4 posts and grow upward through continued condensation until they have filled the entire volume between the 4 posts. These drops come into contact with a drop sitting on air pockets for coalescence by overcoming the pinning forces. However, in the case of macroscopic drops, their coalescence results in a dynamic movement of liquid and the size of the area over which the transition

occurs critically depends on the pinning strength.¹¹⁵ In a further study, Dorer and Ruhe investigated drop condensation on nanorough silicon surfaces coated with polymeric thin films (PFA, PS, PMMA, PEGMEM, PHEMA, and PDMAA).¹¹⁶ They observed that sharp transitions between the wetting states caused different wetting behaviors, even minute variations in the surface energy of the coating material. They observed that even the smallest drops do not penetrate the roughness features, if the condensation conducted onto their superhydrophobic sample surfaces.¹¹⁶

Nosonovsky and Bhushan conducted evaporation/condensation studies of microdroplets on micropatterned superhydrophobic surfaces and concluded that contact angle, contact angle hysteresis (CAH), and transition between wetting regimes are multiscale phenomena.¹¹⁷ Jung and Bhushan offered a criterion for the transition from Cassie¹⁰⁹ (drop on air pockets) to Wenzel¹⁰⁸ (drop immersed between pillars) regimes on patterned surfaces considering water droplet size as an effective parameter with various distributions of geometrical parameters.¹¹⁸ Their experimental results were in good agreement with their proposed criterion. The authors reported that CAH results for the microdroplets having about 20- μm radius showed the same trends with those for the droplet with 1-mm radius due to the decrease in the contact area between the patterned surface and the droplet when the distance between pillars increases.¹¹⁸ Boreyko and Chen showed that condensate drops can be autonomously removed on a superhydrophobic surface made of 2-tier roughness with carbon nanotubes deposited on silicon micropillars and coated with hexadecanethiol.¹¹⁹ Coalesced drops jump out-of-plane with a speed as high as 1 m/s when they gain energy from the surface energy released upon drop coalescence and this property is an advancement to enhance the condensation heat transfer.¹¹⁹ Patankar discussed the micro-/nanofabricated rough surfaces that are being developed for nucleate boiling or dropwise condensation applications.¹²⁰ In boiling applications, rough superhydrophilic surfaces that supply roughness-based cavities or defects provide nucleation sites for vapor bubbles to form and to delay the formation of a vapor film next to the surface. A similar situation is also valid for superhydrophobic surfaces, which enhance dropwise condensation, and the use of pillar geometry with hydrophobic sides and hydrophilic top was discussed.¹²⁰

Liu et al. reported that the final state of the condensed drop was decided by the condition of interfacial free energy such as continuously decreased or a minimum value existed.¹²¹ Drop condensation on a micro-roughened surface prefers a Wenzel state¹⁰⁸ since the interfacial free energy curve of a condensed drop first decreases and then increases, existing at a minimum value. However, in the case of a surface with proper hierarchical roughness, the curve of the interfacial energy of a condensed drop will continuously decline until reaching a Cassie state¹⁰⁹ and a condensed drop on such a hierarchical roughness can spontaneously change into a Cassie state.^{109,121} Chen et al. studied the hierarchical (multiscale) micro-pyramid architecture to supply a significant increase in number density, growth rate, departure rate, and surface coverage of drops for the purpose of the enhancement of dropwise condensation heat transfer.¹²² They showed that both heterogeneous wettability character and hierarchical roughness features in multiscale structures are useful properties and obtained continuous dropwise condensation through the constant activation and mobilization of drops on pyramid-shaped hierarchical structures.¹²² He et al. designed regular poly (dimethylsiloxane) post arrays (fabricated using porous silicon wafers as the template) that had different area fractions of the solid surface in contact with the liquid and reported that if the area fraction of the solid surface in contact with the liquid is equal to or smaller than 0.068, these surfaces maintain their superhydrophobic character when the surface temperature approaches the dew-point.¹²³

Nilson and Rothstein investigated the effect of CAH on the dynamics of the coalescence of sessile drops

on 3 superhydrophobic surfaces having a 150° advancing angle and 3° , 15° , 30° , and 50° CAH values by using Teflon.¹²⁴ It was found that CAH causes a reduction in the deformation of the droplet coalescence and the subsequent mixing. In the case of head-on collisions, an increase in CAH causes a decrease in the frequency resulting in oscillation. Otherwise, in the case of glancing collisions, where a rotation is obtained on the droplet, an increase in CAH causes an increase in the rate of rotation although CAH does not affect the overall angular momentum.¹²⁴ Miljkovic et al. used silicone nanopillar surfaces and investigated the growth and shedding behavior of suspended and partially wetting droplets. They developed a droplet growth model for explaining the experimental results and it was concluded that partially wetting droplets showed 4–6 times higher heat transfer rates than suspended droplets.¹²⁵ Cheng et al. studied drop condensation on a superhydrophobic structure with a 2-tier texture consisting of carbon nanotubes (CNTs) deposited on micromachined posts coated with a fluoropolymer. The authors concluded that adaptive and prompt condensate droplet purging is the main factor for maintaining a long-term dropwise condensation.¹²⁶ Ko et al. fabricated hydrophobic material coated carbon fiber network surfaces made of carbonized polyacrylonitrile (PAN) coated by a hydrophobic siloxane based hydrocarbon, which removed the condensed water easily.¹²⁷ Anderson et al. presented an amphiphilic surface that consisted of densely packed nanowires made of hydrophilic base material with hydrophobic tips, which promotes the periodic regeneration of nucleation sites for small droplets.¹²⁸ Results revealed that this amphiphilic nanointerface produces an arrangement of condensed Wenzel droplets that are fluidically linked by a wetted sublayer where numerous droplets simultaneously merge, without direct contact.¹²⁸

Rykaczewski et al. investigated the role of nanoscale surface roughness on the mechanism of individual droplet formation having water contact angles in the range of 100° to 165° .¹²⁹ The growth mechanism of individual water microdroplets on these surfaces was found to be independent of the surface architecture. They compared experimentally observed drop growth with interfacial free energy values and reported that the base diameter of the observed minimum confined microdroplet is directly dependent to the length scale of the nanoscale surface roughness and the interfacial wetting degree.¹²⁹ Enright et al. studied drop condensation on structured surfaces having length scales ranging from 100 nm to 10 μm to explain the local energy barrier effects on the growth process and the role of nucleation density. The authors found that the effect of the length scale for deciding the wetting state was dictated by droplet nucleation density and with local contact line depinning situation during drop coalescence.¹³⁰

5. Dropwise condensation on self-assembled monolayers

Self-assembled monolayers (SAMs) have a uniform layer of long chain hydrophobic groups when coated on a smooth solid surface by forming a protective hydrophobic layer that has a negligible heat transfer resistance. Such surfaces have been used as model surfaces for the applications in adhesion, wetting, tribology, biocompatibility, and dropwise condensation.^{131–139}

Whitesides and coworkers examined the distribution of condensed water droplets on SAMs of different alkanethiolates on gold and of alkyl siloxanes on glass by optical microscopy to characterize surface heterogeneities.¹³¹ Kumar and Whitesides prepared patterned surfaces consisting of hydrophobic and hydrophilic regions and having micrometer-scale periodicities by using SAMs coated on gold. They monitored the drop condensation process under constant relative humidity conditions and found that SAMs are very sensitive to relative humidity and this technique is useful for studying phenomena such as drop nucleation, CAH, and spontaneous dewetting and break-up of thin liquid films.¹³² Das et al. investigated SAMs created where chemisorption of alkylthiols was applied as monolayers and, due to their negligible thickness, SAMs

show negligible resistance to heat transfer but caused an increase in condensation heat transfer coefficient of about 4–5-times under 10 kPa vacuum conditions.¹³³ Hofer et al. investigated microdroplet condensation on flat Ta₂O₅ surfaces modified by SAMs. They used condensation figures to evaluate the surface qualities such as homogeneity/heterogeneity and microdroplet density.¹³⁴ Pang et al. used SAMs made of 1-octadecanethiol and 16-mercaptohexadecanoic acid that were adsorbed onto gold-coated copper substrates and related the heat transfer coefficient to changes in SAM monolayer thickness and chemistry. The authors found that dropwise condensation formed by using octadecanethiol SAM is a dynamic process in that the heat transfer coefficient decreases with time over 2 h.¹³⁵

Vemuri et al. used SAMs of n-octadecyl mercaptan and stearic acid on copper alloy surfaces as hydrophobic coatings with the aim of enhancing steam condensation through dropwise condensation.¹³⁶ It was found that n-octadecyl mercaptan coated SAM surfaces increased the condensation heat transfer rate by a factor of about 8-times when operated under atmospheric conditions and a theoretical model was developed involving the effect of interfacial heat transfer coefficient on heat transfer rate to calculate the sweeping effect of large falling drops.¹³⁶ In a further study, Vemuri et al. used 2 different types of SAM coatings (stearic acid and n-octadecyl mercaptan) for a period of more than 2600 h. An oxide layer was formed between the substrate and SAM surface to enhance the bonding ability of SAMs to the substrate and to improve the life-time of the coatings and it was concluded that n-octadecyl mercaptan SAM showed good dropwise condensation due to its covalent bonding with the substrate surface when compared to that of stearic acid SAM, which is bonded to the substrate surface by only hydrogen bonding.¹³⁷ Leu and Wu studied the movement of a droplet on a vertical surface created by energy patterning process using 1-dodecanethiol SAM coated onto a hydrophilic silicon substrate to improve heat transfer efficiency in a vapor condensing system and obtained 10% higher heat transfer efficiency.¹³⁸

Lan et al. examined the effect of surface free energy and nanostructures on dropwise condensation using SAM coatings of n-octadecylmercaptan on copper substrates with/without nanostructures.¹³⁹ Heat transfer characteristics were determined by conducting steam condensation experiments on a vertical plate. Experimental results showed that the nanostructured SAM coated surface did not enhance the dropwise condensation heat-transfer performance due to the increase in condensing surface area, compared to the mirror-polished SAM coated surface, and this conclusion was attributed to the possibility of the nanostructure's retarding effect on the condensate film.¹³⁹

6. Pattern formation from breath figures

Hexagonal ordered structures on a surface can be formed by evaporating polymer solutions in a volatile solvent, such as carbon disulfide, benzene, or chloroform in the presence of moisture with forced airflow across the solution surface. Tiny droplets condense on the polymer surfaces¹⁴⁰ and when the solvent and water droplets evaporate completely, a hexagonal air-filled packed array of holes is formed on the surface of the polymer. The breath figures method has been used as an alternative to the conventional templating and lithographic techniques for structuring surfaces where the need for very specialized machinery is avoided. These hexagonally arranged pores are known as honeycomb structured porous polymer films/membranes and are applied in many fields such as photonics, optoelectronics, filtration, superhydrophobic and self-cleaning surfaces, cell culturing and scaffolds for tissue engineering, bioassays, templates for soft lithography, iridescent or biomimetic materials, catalysis, optics, filtration cell culture, coatings, nano- and micro-reactors, and diagnostic kits.^{141–144} It is possible to obtain mono- or multi-layered polymeric membranes of various pore sizes by tuning variables including polymer

type, molecular weight, solvent, polymer concentration, relative humidity of the medium, and temperature.

The materials used in the breath figures as a templating method can be classified into 4 categories: (i) homopolymer; (ii) copolymer; (iii) amphiphilic polyion complex; (iv) organic/inorganic hybrid. Humidity is the main factor that controls the pore size and the sizes of the holes increased with the increase in humidity due to coalescence of water droplets. However, excessively low humidity impairs water condensation while very high humidity leads to pores with a wide range of sizes due to coagulation of the rapidly condensing droplets. Meanwhile, higher polymer concentration in the polymer solution results in smaller pores and thicker walls. The casting volume of the polymer solution can also be varied to control the pore size. The substrate can be cooled prior to the casting and this decrease in temperature suppresses solvent evaporation, leading to bigger water droplets and therefore bigger pore size.^{141–144}

The most common polymer used in the breath figure technique is polystyrene (PS) and its derivatives.^{145–197} In addition, polymethylmethacrylate (PMMA),^{151,195,196,198–200} polylactic acid (PLLA),^{201–206} polydimethyl siloxane (PDMS),^{207–209} and some other polymers^{210–228} can also be used in this technology. Breath figures can be obtained by applying several different methods such as: (i) flowing humid air to the polymer solution surface;^{145–180,200,202,208,210–219} (ii) forming breath figures in static conditions;^{181–192,198,201,203–207,209,220–224} (iii) emulsification technique;^{157,193} (iv) spin/dip coating.^{194–197,225–228} The most common dynamic technique used in the literature is to send the humid air to polymer solutions where water vapor is introduced to the surface of the polymer solution by flowing moisturized air at a specific rate, which is usually produced by bubbling inert carrier gas through water. A temperature gradient occurs between the surface of the polymer solution and the bulk. The desired humidity conditions for the fabrication of breath figures can be obtained by adjusting the velocity of the air flow.^{145–180,200,202,208,210–219} In the static method, honeycomb patterned porous films from breath figures can also be obtained where no dynamic moisture air flow is sent to the medium. Solvent evaporation of the casting polymer solution is generally conducted inside a sealed chamber or in room conditions where moist air is present with a stable relative humidity and temperature.^{181–192,198,201,203–207,209,220–224} The emulsification technique is another method for the fabrication of breath figures where water (or an aqueous solution) is directly added to a polymer solution sometimes containing particles. Then the system is generally homogenized by sonication after adding.^{157,193} Spin/dip coating in humid conditions was also applied to obtain breath figures where elongated pores rather than circular ones were formed. Highly regular porous structures can be obtained by applying high spinning rates since low spinning rates lead to coalescence of condensed droplets.^{194–197,225–228}

6.1. Breath figures patterning using polystyrenes

6.1.1. Moisturized airflow technique in breath figures patterning method

PS and its derivatives were used many times in the breath figure technique.^{145–197} Most researchers preferred to apply dynamic moisturized airflow. Widawski and François published the first report on breath figure templating for PS and PS-polyparaphenylene block copolymers to obtain honeycomb membranes using CS₂-polymer solutions under humid conditions in 1994. They could control both the size distribution and relative positions of the pores. The authors reported that regular pore sizes and optimization in their structures including thicknesses of their walls are thought to enhance the mechanical properties and efficiencies of membranes. They proposed that these membranes can be used for the control of drug release, in optical applications, and as scaffolding materials, etc.¹⁴⁵ François and coworkers investigated a set of 6 branched polystyrene

star polymers having different molecular weights and reported that honeycomb membranes could be obtained by considering key factors such as branching density, molecular weight, and solution viscosity.¹⁴⁶ Pitois and Francois prepared regular micro-porous polymeric membranes by evaporating polystyrene in 1,2-dichloroethane solution and condensation of water vapor on these surfaces. They investigated the driving force to form these regular polymeric structures and concluded that the driving force is the ability of polymer precipitation at the interface, which was related to the star-polymer microstructure.¹⁴⁷ Karthaus et al. reported a study on the formation of ordered micron-sized honeycomb structures with 4 different kinds of materials: an amphiphilic polyion complex, a PS-block-polyisoprene copolymer, a mixture of a TiO₂ precursor with a low molar weight amphiphile, and PS. They found that high humidity is needed for the formation of honeycomb structures.¹⁴⁸

Srinivasarao and coworkers formed ordered structures by evaporating solutions of an atactic PS polymer with one end terminated by a carboxylic acid in a volatile solvent and in the conditions of moisture with forced air flow across the solution surface.¹⁴⁹ They reported that the dimensions of the bubbles can be controlled by changing the velocity of the air flow across the surface and when a solvent less dense than water, e.g., benzene or toluene, was used, then the hexagonal array formed but, if a solvent denser than water, e.g., carbon disulfide, was used then only a single layer of pores was formed and a 3D array could not be produced, contrary to the literature. The importance of this work is its advantages of easy production and easy pore control (by changing the velocity of the air flow) of these kinds of ordered structures using simple polymers and production of pore dimensions comparable to the wavelength of visible light.¹⁴⁹

Stenzel proposed that it is necessary to use spherical PS polymers, which can be easily produced by controlled radical polymerization techniques, to obtain a high regular honeycomb ordering. The size of the pores in the structured porous films were dependent on the casting conditions together with the type of polymer used.¹⁵⁰ Peng et al. used PMMA, linear PS without any polar end group, and crown ether-containing series such as PS-crown-PS and PMMA-crown-PMMA for the fabrication of 2D ordered structures with uniform hole size by the evaporation of polymer solution in a humid environment. The importance of polymer and humidity has been emphasized for the production of regularly ordered structures. With this study, the authors also discussed the reasons for the selection of hexagonal packing instead of other packing kinds and attributed this behavior to its having the lowest free energy.¹⁵¹ Peng et al. also examined the various factors influencing the pore formation process and hole sizes such as polymer molecular weight, solvent properties, and humidity to gain a better understanding of the pore formation mechanism.¹⁵² PS having different molecular weights and toluene, chloroform, carbon disulfide, and tetrahydrofuran solvents were studied. Results showed that a strong linear correlation existed between the atmospheric humidity and pore sizes, e.g., higher humidity leads to larger pores.¹⁵²

Stenzel and coworkers used modified cellulose and statistical poly(S-co-2-hydroxyethylmethacrylate) copolymer backbones for the formation of porous films. They prepared comb polymers using RAFT polymerization via a Z-group approach since the R-group approach results in some broadening of the molecular weight distributions, which is undesirable. Then they used these comb architectures as substrates for porous film formation. A correlation was observed between branch length of the combs and the quality of the hexagonal orders of honeycomb structured films. An increase in regularity was observed with an increase in the number of branches on a backbone and length of the PS branch.¹⁵³ Cui et al. used blends of PS and poly(2-vinylpyridine) (PVP) as a model system since they have very different chemical characters in pattern formation. In the case of a high relative humidity environment, water droplets assembled into hexagonal arrays and the PVP domains were reassembled by the water droplets template. A transition in the topography from the island-like to holes

was seen with an increase of humidity. The authors reported that humidity, weight ratio of PS/PVP, and PS molecular weight played a significant role in the formation of the regularly ordered holes.¹⁵⁴ Zhao et al. successfully fabricated ordered porous membranes from random poly(S-co-acrylonitrile) in tetrahydrofuran solvent by the breath figure method. It was found that humidity, concentration of solution, and temperature affected the membrane morphology. Pore size and the patterns were also affected by these influencing factors. An increase was observed in pore sizes with an increase in RH while they decreased with an increase in solution concentration. They also pointed out the importance of the polar group for the stabilization of water droplets in the case of water miscible solvents such as tetrahydrofuran.¹⁵⁵

Stenzel and coworkers used amphiphilic block copolymers of PS where a suborder on the nanoscale can be introduced, which can be used for cell growth applications. They stated that honeycomb-structured porous films can easily be prepared with breath figures and the casting process promotes amphiphilic blocks preferentially exhibited at the pore surface. This kind of honeycomb structure may be found itself in application areas such as microreactors for the desired covalent attachment of compounds on the pore surfaces. This process also supplies a versatile way for the production of films having regularly ordered pore diameters changing from 150 nm up to 10 μm .¹⁵⁶ Stenzel and coworkers also investigated the 4 different casting parameters (airflow, using cold stage, casting on water, and emulsion methods) to see the possibilities and limitations to fabricate honeycomb structured porous materials. They altered the film qualities by changing the architecture and composition of polymer using linear, star, and comb PS as well as an amphiphilic diblock copolymer composed of PS-block-poly(dimethylacrylamide) and found that linear PS usually forms low quality films and irregular pore formation; however, amphiphilic copolymers could not give regularly structured films over time using casting on water and emulsion techniques. The authors attributed this behavior to interactions between the hydrophilic block and water droplets. This study highlights the honeycomb structured porous film generation by declaring the facilities and restrictions to the water assisted templating method.¹⁵⁷

Later, Yabu and coworkers reported a simple production method for structuring honeycomb patterned metal films by electroless plating. They prepared honeycomb structured films by casting chloroform solutions of PS and pincushion structures were obtained by peeling off the top layer of the former films. They observed Ag deposition on the honeycomb patterned films from XPS analysis and obtained metal mesoscopic structures after thermal decomposition or solvent elution of the template polymer. These unique metallic structures by honeycomb and pincushion polymer films have many advantages than other microstructured films reported in the literature, which had lower refractive indexes, lower electrical conductivity, and lower chemical and mechanical stability.¹⁵⁸ The breath figure method was used for patterning silica microbeads on PS polymer films with ordered arrays of pores by Lu and Zhang. They controlled pore sizes of the honeycomb structured films by changing the polymer composition and these pores served as a template for the microbeads, which were patterned on the polymer films where honeycomb membranes containing microbeads have potentials for both detection and sensing applications.¹⁵⁹ Park et al. prepared hierarchically ordered polymeric structures by the imposition of physical confinement via various shaped gratings. A monocarboxy terminated PS was used for this purpose. The authors applied polymeric surfactant to enhance interfacial wetting and hierarchical structures without defects. Well-ordered hierarchical structures were obtained after the evaporation of solvent.¹⁶⁰

Wong et al. synthesized a set of amphiphilic block copolymers of PS-b-poly(N,N-dimethylacrylamide) and investigated block size effects on the pore sizes. They showed that the regularity of the pores was mostly affected by the RH of the medium. Regular pores cannot be obtained at very low (below 50%) and at elevated (above 80%) RH and pores were found to be more hydrophilic than the surface since they were created by

encapsulation of the water droplets.¹⁶¹ Zhang et al. fabricated a porous PS film having an ordered pore structure for the purpose of using it as a template for patterning proteins. They used amino-terminated PS and fluorescein-isothiocyanate-conjugated bovine serum albumin was attached to the pores of the surface of the PS through cross-linking of glutaraldehyde. This application can be used as a non-lithographic method for 3D protein micropatterning, which is important in tissue engineering, and protein- and cell-based biosensors.¹⁶²

Zander et al. transferred arrays of pillars (inverse pores) to polymeric films by using them as templates to obtain textured silicone pillars and breath figure templating was proposed as a new technique for fabrication of hydrophobic surfaces, providing a low cost alternative to customary techniques.¹⁶³ Hernandez-Guerrero et al. applied graft copolymerization and used PS-PHEMA based honeycomb membranes and a thermoresponsive polymer, PNIPAAm, inside the pores to form a membrane to be used in fibroblast cell attachment. The interior of the pores of the membranes was rich in PNIPAAm while the surface was made of PS. Porous films display a switchable structure as hydrophilic/hydrophobic characteristics that were different from those of the usual porous ungrafted films. After the experiments on the attachment of fibroblast cells, they concluded that a better interaction between cells and the surface exists for higher hydrophilicity.¹⁶⁴

Bolognesi and coworkers proposed that breath figure compact structure is suitable for the fabrication of elastomeric stamps since they do not lose their shape after printing. They first formed hexagonal ordered patterns fabricated from the breath figure method on a PS with micron sized holes on the surface; then PDMS was used to obtain a positive mold to create replicas and also can be inked with a convenient biomolecule solution.¹⁶⁵ Cai and Newby investigated the fingering instability of the water layer by Marangoni flow using PS and porous films with hexagonal and square pore arrays. In this method, not only hexagonal arrays but also square and other types of arrangements of pores in the films can be achieved and this opens a new way to manufacture highly ordered porous structures in a wide diversity for use in lithography masks, biomolecular patterning, and metal or metal oxide patterning.¹⁶⁶ Kojima et al. investigated the effect of interfacial tension between water and polymer solution for the control of the honeycomb pattern structure by using PS and amphiphilic copolymers. The physical properties of these amphiphilic copolymers play a critical role in the stabilization of the condensed water droplets and structure of the honeycomb patterned films. The uniform structure of the micropores of the honeycomb patterned film increased with a decrease in the interfacial tension value. In addition, the thickness of the honeycomb patterned film decreased with a decrease in the interfacial tension value.¹⁶⁷ Munoz-Bonilla et al. combined the “top-down approach” (e.g., the breath figures method to produce porous microstructures) with the “bottom-up” approach (block copolymer self-assembly to induce microphase separation at the nanometer length scale) for the preparation of hierarchically micro- and nanostructured polymer surfaces using polypentafluorostyrene, and methacrylate based block copolymers. They reported that their surface chemical composition can be altered by annealing in dry or humid air. Annealing can also reversibly modify topography and nanostructuration. They also noticed that when these films are exposed either to air or to tetrahydrofuran vapor, the nanostructure of the pores can be arranged from a micellar array to a lamellar phase.¹⁶⁸

Billon et al. reported an easy method to produce ordered structures on different polymeric substrates such as a flexible PVC sheet or rigid PMMA plate by using PS that was synthesized with one chain end ionic functionality in a one-step reaction by nitroxide-mediated polymerization and prepared in CS₂ solutions. They investigated different experimental parameters' (polymer concentration or wet thickness) effects on pore size and thus the resultant honeycomb morphologies.¹⁶⁹ Sun and coworkers applied a one-step process by using a surfactant-encapsulated polyoxometalate in a PS solution to obtain hole-containing microporous PS films. The

accumulation of the surfactant in these pores was achieved and an ordered and tight lamellar structure was obtained. This porous honeycomb patterned hybrid film showed intense red emission in UV light. In addition, it was shown that metal and magnetic nanoparticles have been successfully introduced into the microporous structure, which can be applied in the sensor, separation, and catalysis fields.¹⁷⁰ Escale et al. used poly(*n*-butyl acrylate)-block-PS and poly(*tert*-butyl acrylate)-block-PS copolymers to obtain a honeycomb morphology controlling by solvent evaporation under humid atmosphere conditions. As a second step, structuring was provided by diblock copolymers chosen for their ability to self-assemble into ordered nanophases. It was found that the properties of the copolymer, such as interaction parameter, glass transition temperature, and monomer weight fraction affect both the micrometric pore organization and the internal nanoscale morphology of the diblock copolymer self-assembly.¹⁷¹

Galeotti et al. reported 2 simple approaches for the fabrication of micropatterned functionalized polymer films. In the first, they obtained honeycomb membranes with pores enriched with amino groups by using amino-terminated linear PS. In the second, a luminescent chain-ended PS was synthesized to demonstrate how the honeycomb structured film can be transformed into a flat micropatterned fluorescent film. Both of the films can be used in biological tests reacting with other molecules to create more complex structured arrays.¹⁷² Hirai et al. created biomimetic bifunctional surfaces having antireflective and superhydrophobic properties using honeycomb structured PS and polyacrylamide derivative films as dry-etching masks. Their flexible nature opens up an application area for curved surfaces. This is also a simple method to produce organized structured surfaces that could be used as solar cells.¹⁷³ Ke et al. synthesized bioactive films that have potential applications as templates, picoliter beakers for bioanalysis, and cell culture materials from glycopolymers based on (PS-co-acetylglucosyloxy ethyl methacrylate) with well-defined linear and/or comb-like structures. Structure of the polymers and concentration of the solutions highly affected the regularity and pore size of the films.¹⁷⁴ Ke and coworkers grafted carbohydrate monomers to an amphiphilic block copolymer, PS-block-(2-hydroxyethyl methacrylate), for the production of self-organized honeycomb-patterned films by the breath figure method. It was found that hydroxyl groups aggregated mainly inside the pores by the help of the 3D fluorescence measurements, which give a change of site-directed surface segregation. FTIR, XPS, SEM, AFM, and contact angle measurements confirmed site-directed growth of the glycopolymer chains.¹⁷⁵

Min et al. grafted NIPAAm and *n*-acryloyl glucosamine glycopolymer chains on the honeycomb structures that were made of PS-co-maleic anhydride. It was shown that surface grafted groups increased the wettability depending on the temperature.¹⁷⁶ Sharma et al. suggested a transport model to understand the effect of the solvent and airflow in designating the rate and extent of evaporative cooling and they compared their model results with the corresponding experimental measurements for PS/CS₂ solutions. They pointed out that solvent evaporation rate, polymer concentration, and temperature of polymer solution have an influence on the morphology achieved to explain how the pore size depends RH, temperature of air, velocity, choice of the polymer, and solvent.¹⁷⁷ Amirhkani et al. conducted systematic experiments to reveal the effect of different stabilizers on the porous honeycomb structure in the case of identical physical conditions. Results showed that a large area of regular spherical bubbles can be fabricated by using an end-functional polymer. Meanwhile, adding particles to the polymer solution presented smaller arrays of the flattened bottom bubbles. It was concluded that the end-functional polymer is more suitable for pattern formation.¹⁷⁸

Ferrari and coworkers investigated the role of solvent in the process of breath figure formation using linear PS solutions. They pointed out that polymer–solvent interactions were the key parameter for pattern formation. In addition, miscibility, boiling point, and boiling enthalpy were found to be other important

parameters.¹⁷⁹ Wan et al. prepared membranes from PS-block-poly-(N,N-dimethylaminoethyl methacrylate) at the interface of air/ice, which can be extended to the interfaces of air/glycerol and air/formic acid. They presented a static model for the calculations of critical pressure to destroy the film. The authors suggested that these highly uniform membranes can be used in many fields such as high-resolution and energy-saving separation processes.¹⁸⁰

6.1.2. Breath figures patterning experiments in static conditions

Boker et al. used the combination of 2 self-assembly processes: self-assembly into a well-ordered hexagonal array by breath figures on the surface of PS–chloroform polymer solution and self-assembly of CdSe nanoparticles at the polymer solution–water droplet interface at 80% RH and room temperature. They showed that CdSe nanoparticles preferentially segregated at the polymer solution–water droplet interface by forming a 5–7-nm-thick layer serving as functional walls of the holes and proposed that this process opens up a new possibility for the usage of these structures in sensory, separation membrane, or catalytic applications.¹⁸¹ Cui et al. distributed poly-2-vinylpyridine (PVP) in the holes of PS for the production of honeycomb macroporous films that display a reversible property by responding to water and various solvent vapors by using breath figure technology at 30% RH and 25 °C. They observed that, after the treatment of the porous film with water, the honeycomb pattern would turn into a hexagonal island like pattern. In contrast, after heating for the removal of water, honeycomb patterns were seen again. This reversible property was also observed when organic solvents were used. They obtained ordered island like patterns by using carbon disulfide, toluene, and THF solvent vapors, while ethanol, chloroform, methyl ethyl ketone, and dimethyl formamide solvent vapors resulted in honeycomb morphology.¹⁸²

Bolognesi and coworkers examined the structural parameters of PS such as molecular weights, polydispersities, and carboxylic terminations on pattern formation properties by breath figures at 20–40 °C. Dicarboxy-terminated PS resulted in a highly regular honeycomb microstructured morphology indicating the importance of the fundamental role of the polar groups on pattern formation. The authors reported the advantages of 3-dimensional patterned surfaces as photonic crystal materials.¹⁸³ Stenzel and coworkers used a thermoresponsive block copolymer, PS-block-poly(N-isopropyl acrylamide), which was cast on a cold glass surface at 50% RH and –10 °C, and found that the pores were enriched in hydrophilic parts, resulting on stimuli-responsive behavior. They proposed that the resulting structure may serve as a way of producing reactive functional groups present in the pores while the remaining surface is unreactive.¹⁸⁴

Ghannam et al. presented a new method to obtain ordered structures using self-assembly of ionomer macromolecular systems. They spread out ionomer solutions over organic and inorganic surfaces. They concluded that a more regular organization was obtained on mica than on glass and this result may be attributed to the interactions between cationic ionomer ends and oxanions of the mica surface. They produced highly organized hexagonal patterns on poly(vinyl chloride).¹⁸⁵ Dong et al. fabricated honeycomb-structured microporous films from a hyperbranched poly(3-ethyl-3-oxetanemethanol)-star-PS multiarm copolymer by evaporation of chloroform solution at 70% RH and room temperature where the size of the pores could be easily controlled by altering the casting volume of the solution, molecular weight, and concentration of the polymer.¹⁸⁶

Li et al. prepared PS-b-polybutadiene-b-PS (SBS) micro-patterned polymer films by using a commercially available block copolymer. These patterned films were obtained by evaporating SBS/carbon disulfide solutions with different concentrations under high RH conditions in a glass vessel at room temperature. Random pore arrays were obtained instead of regular ones with an increase in the concentration of the solution. Porous

structures were well preserved and thermal and chemical resistance of the films was significantly enhanced owing to the cross-linkage in the following UV irradiation. The authors reported the beneficial effects of the photochemical process and pointed out that the formation of polar groups on the film surface alters surface wettability from hydrophobic to hydrophilic and the resulting films were non-cytotoxic and suitable for cell scaffolds.¹⁸⁷ Li et al. reported highly ordered cross-linked PS thin films by using the breath figures method. The thermal stability and solvent resistance of the UV cross-linked films improved significantly; in addition, the surface became hydrophilic due to the introduction of polar groups during UV exposure, which is desirable in biomaterial applications.¹⁸⁸ Li et al. also fabricated honeycomb structured films from PS-block-polyacrylic acid (PS-b-PAA) amphiphilic diblock copolymer at saturated humidity in a vessel at room temperature. They cross-linked both PS and PAA parts efficiently by applying simple UV irradiation. Both thermal and solvent resistances of the film were improved after UV exposure and well-ordered 3D structures were obtained. A change in wettability was observed on the surface of the film from hydrophobic to hydrophilic due to the formation of polar groups during the photochemical process.¹⁸⁹ Li et al. also used PS-b-PAA block copolymer to fabricate a honeycomb structured gold mask by sputter-coating a micro-porous polymer film and then these patterns were transferred onto silicon wafers. They reported that the large etching rate selectivity between golden mask and substrate plays a crucial role in the effective transfer of the patterns. They also reported that fabricated micropatterns on solid substrates could be replicated by PDMS stamp. This facile method presents new views in the field of patterning on a micro scale and applications of templates without the requirement of photolithography.¹⁹⁰

Ting et al. produced porous films using a block copolymer based on PS and a glycopolymer by applying the breath figure method at 67% RH and 23 °C. Galactose moieties on the surface could serve as drug delivery carriers to target liver hepatocytes in the body, which conjugate strongly to galactose. Galactosylated porous films on protein patterning could also be used as a screening device.¹⁹¹ Xiong et al. studied the use of linear PS and star-shaped PS-block-polybutadiene copolymer solutions that have been cast in a static humid environment and investigated the influence of the flow ability of polymer solution and water vapor pressure on the final film structure by using different starting polymer concentrations at 4 to 90 °C. They found that higher solvent vapor pressure would be required for the fabrication of ordered patterns having smaller pores and initial polymer concentration has an important effect on the packing of condensed water droplets since the polymer solution could reach a level of 'solidification' during a reasonable time of solvent evaporation that fixes the droplets and prevents the droplets from coalescing.¹⁹²

6.1.3. Emulsification technique in breath figures patterning method

Stenzel and coworkers applied an emulsification method to fabricate honeycomb structured porous materials using linear PS and PS-block-poly(dimethylacrylamide) copolymers. They added Milli-Q grade water to polymer solutions and sonicated them using an ultrasonic bath for 30 s for sufficient dispersion of the system. Each emulsion was then cast onto a glass cover slip under ambient conditions and at 68% RH to produce the porous films.¹⁵⁷ Sun et al. studied the particle-assisted fabrication of honeycomb structured hybrid films using silica, PS particles, and poly(N-isopropylacrylamide)-co-acrylic acid microgel particles in facilitating breath figure array preparation and it was concluded that inorganic particles, polymeric particles, and microgels can be used to serve as stabilizers in the breath figure method. The authors claimed that this particle assisted, bottom up surface patterning technique has great potential for the production of functional porous structures.¹⁹³

6.1.4. Spin/dip coating technique in breath figures patterning method

Hiwatari et al. applied dip coating of a graft copolymer prepared by free radical polymerization of a poly(ethylene glycol) macromonomer and styrene using AIBN as radical initiator in ethanol/water solvent for the production of well-controlled polymeric honeycomb structures. They pointed out the importance of humidity control for the fabrication of an ordered porous structure and the solution concentration effect on the penetration of the pores into the substrate.¹⁹⁴

Park and Kim produced breath patterns on a homopolymer film of cellulose acetate butyrate, monocarboxylated end-functional PS, and PMMA by spin coating of polymer solutions using various solvents under dry condition and produced patterns in a dry environment (RH less than 30%) for the first time. A small amount of water was added to a water-miscible solvent of tetrahydrofuran to create a humid environment, where THF is a good solvent for the given polymers. They changed the water content in THF solution and rate of rotating of the spin coater for controlling pore sizes from hundreds of nanometers to several micrometers. It was proposed that cellulose acetate butyrate can be used as cell culture substrate due to its high clarity, mechanical strength, and good biocompatibility properties.¹⁹⁵ Madej et al. used PS and PMMA blends dissolved in THF/water mixtures and the results showed that the composition of spin-cast polymer film is more important than the effects of ambient atmosphere. Such production of multicomponent polymer films with hierarchic morphology was proposed to be useful for generating photonic waveguides, OLED displays, or protein chips.¹⁹⁶ Li et al. reported the formation of a highly ordered microporous film by breath figure methodology using polymethylene-*b*-PS polyolefin diblock copolymers in CS₂ under a humid atmosphere. They examined the effects of molecular weight, RH, and temperature on the film morphology and reported that the length of the PS segment plays an important role since a pothole like structure was obtained instead of a honeycomb structure when using PM-*b*-PS with the shortest PS segment.¹⁹⁷

6.2. Breath figures patterning using polymethylmethacrylates

PMMA is also an important polymer for the application of breath figures patterning.^{151,195,196,198–200} Haupt et al. used a statistical copolymer of MMA with a trimeric hexafluoropropyleneoxide substitute containing methacrylate to fabricate polymer arrays on semiconductor surfaces. They converted the polymer honeycombs into etch resistant metallic disk structures and appropriate metallic nets or grids via metal deposition and lift-off techniques. Metallic disk structures were used for etching 2-dimensional photonic crystals out of silicon and the metal grid was used as a dichroic filter with an optical transmission bandpass in the infrared region of the spectrum.¹⁹⁸ Connal et al. prepared star-microgels and used them for the production of honeycomb films. Living linear PMMA was reacted with ethylene glycol dimethacrylate (EGDMA) cross-linker and MMA as spacer to produce star-microgels. This study is the first report that shows the use of well-defined star-microgels in the production of highly ordered porous films. It was observed that a decrease was determined in the pore diameters with an increase in the number of PMMA arms and molecular weight of the star-microgel.¹⁹⁹ Wong et al. used silicon based random branched copolymers such as PEGDMA-ran-PMMA-ran-poly[3-(trimethoxysilyl) propyl methacrylate] and PEGDMA-ran-PMMA-ran-poly{3-[tris(trimethylsiloxy)silyl] propyl methacrylate} for the production of breath figures. It was revealed that these films can be adjusted according to the changes of casting conditions and concentration ratios of PMMA to PMPS or PMMA to PTRIS in the copolymer compounds used during the formation of porous films that can be applied as thermal sensors or cheap digital displays when used with materials such as thermal/light emitters in the pores of the films.²⁰⁰

6.3. Breath figures patterning using polylactic acid derivatives

Hydrophilic polymers were also tried for the breath figures patterning method to be applied both as a cell culture substrate and scaffolds for tissue engineering. Zhao et al. fabricated ordered micrometer-size honeycomb structures using random poly(d,l-lactic-co-glycolic acid) (PLGA) by a solvent casting process. They also obtained a honeycomb-like structure by adding polyethylene-block-poly(ethylene glycol) into the solution of the PLGA solutions. The authors concluded that the distribution of the sizes and arrangement of the pores depends on the hydrophilicity of film formation material and process conditions such as concentration and atmospheric humidity.²⁰¹ Karikari et al. used well-defined 4-arm star-shaped poly (D,L-lactide) (PDLLA) for the production of honeycomb structures. They investigated the relationship between molar mass, viscosity of polymer solution, and pore dimensions. An increase in the average pore dimensions was observed when PDLLA molar mass increased and polymer solution concentration decreased. A linear relationship was found between RH and average pore dimensions.²⁰² Tian et al. investigated the compatibility of 7 different solvents with poly(phenylene oxide) and PLGA polymers for the formation of honeycomb structures and the influence of the solvent boiling points on the regularity of the patterns. It was found that the volatility of the solvent is not only responsible for the regularity of the porous structure but also influences the pore sizes of the honeycomb films. On the other hand, effects of mixed solvent on pattern formation were also examined by mixing different kind of solvents.²⁰³

Tian et al. investigated the effect of solution concentration on pattern fabrication using amphiphilic poly(L-lactide)-block-poly(ethylene glycol) (PLEG) in high-humidity conditions. The authors pointed out the importance of bioactive PLEG honeycomb polymeric film usage in cell culture and tissue engineering.²⁰⁴ Fukuhira et al. used PDLLA and dioleoylphosphatidylethanolamine (DOPE) surfactant for the stabilization of water droplets during evaporation in the breath figure process. DOPE is an efficient surfactant for the fabrication of honeycomb-patterned film formation since it has a low HLB value and can maintain high interfacial tension (>10 mN/m) during evaporation of chloroform.²⁰⁵ Jiang et al. used Ag nanoparticles as a promoter for the formation of breath figure arrays on polyurethane and PDLLA surfaces for the first time and found that the breath figure technique can be transferred to dry conditions with the help of Ag nanoparticles that assembled at the liquid-liquid interface.²⁰⁶

6.4. Breath figures patterning using polydimethylsiloxanes

Gau and Herminghaus fabricated ordered aqueous breath figures in hexagonal shapes by thermal evaporation of calcium chloride as a polar compound through a suitable mask onto a hydrophobic silicon rubber substrate under high vacuum. They found that 4-droplet coalescence cascades were dominant for the formation of perfectly hexagonal breath figure structures.²⁰⁷ Connal et al. produced porous honeycomb morphology polymer films on nonflat surfaces by using a highly branched star polymer with PDMS functionality that can be used as soft lithography templates. PDMS was selected because of its low Tg and soft nature, allowing reproduction of the TEM grid contours.²⁰⁸ Shojaei-Zadeh et al. reported a procedure where water droplets nucleate and grow on a liquid PDMS film due to condensation from saturated vapor to provide a uniform, ordered, and mechanically stable macro-porous membrane.²⁰⁹

6.5. Breath figures patterning using other polymers

Yabu and coworkers used polyion complexes of polyamic acids and dialkylammonium salt to obtain honeycomb structures having high thermal and chemical stability to be used in the fields of electronics, photonics, and

biotechnology. They converted the polyion complex film to the polyimide, applying a simple chemical treatment preserving the porous structure.²¹⁰ Niskikawa et al. fabricated anisotropic patterns from poly(ϵ -caprolactone) by stretching and transforming the array of hexagonal micropores into anisotropic alignment of stretched micropores. Hexagonal, rectangular, square, and triangular geometric patterns could be obtained on the stretched film, which can be used as a cell culture substrate.²¹¹ Srinivasarao and coworkers reported hexagonally ordered 2-dimensional microstructured films made of rod-like conjugated poly(para-phenylene ethylene) and found that it is necessary to use either highly branched or coiled (such as PS) structural segments.²¹²

Yabu and coworkers used a fluorinated copolymer to obtain optically transparent and superhydrophobic sub-wavelength-pore honeycomb patterned films having a pore size of 20 nm.²¹³ In a further study, they used fluorinated microporous polymer film to give superwater- and oil-repellent surfaces by self-organization. These films can be used for dust-free, low friction coatings.²¹⁴ Yabu and coworkers also used a photo-crosslinkable oligomer and an amphiphilic copolymer to obtain cross-linked honeycomb patterned micro-porous films by UV irradiation. They stated that these films can be used for membrane filters and microreactors.²¹⁵

Beattie et al. fabricated honeycomb membranes of PS-b-polyacrylic acid templated with polypyrrole, which will be used as a scaffold for cell growth, and it was observed that attachment and growth of the fibroblast cells were affected by the porosity of these films where cell attachment was enhanced by smaller pore sizes.²¹⁶ Pintani et al. used polyfluorene copolymer and fabricated an elastomeric PDMS replica of breath figure pattern as the master to obtain microstructured organic light emitting diodes (LEDs). Due to the current and power efficiency being higher than those of non-patterned devices, the procedure introduced in this paper has significant potential for organic device fabrication without the requirement of a complicated subtractive patterning process.²¹⁷ Zhao et al. reported the synthesis of honeycomb ordered polycarbonate films in chloroform, dichloromethane, and tetrahydrofuran. Pore sizes increased with RH and decreased with an increase in polymer concentration. Ordered polycarbonate films may have an application in electronics, optics, etc. due to their good mechanical and optical properties.²¹⁸ Bolognesi and coworkers presented a methodology for turning a conjugated copolymer based on polyfluorene bearing tetrahydropyranyl groups into a solvent-resistant material after an appropriate thermal treatment, for use in the preparation of insoluble nanoporous and honeycomb-structured films.²¹⁹

Maruyama et al. used a variety of amphiphilic polymers including functional polymers, such as DNA/amphiphile complexes, saccharide-containing vinyl polymers, electrically conducting polythiophene complexes, or photoresponsive azobenzene-containing complexes for the production of mesoscopic honeycomb structured patterns by a simple solution casting process. It was concluded that size and structure of the patterns can be arranged by concentration, atmospheric humidity, etc.²²⁰ Yu et al. fabricated an ordered honeycomb structure using 4-dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANI) via a water-assisted self-assembly method for the first time. Production of the 3D ordered macroporous structures from conducting polymers opens up new applications in electronic and electrochromic devices.²²¹ Xu et al. prepared micron sized cellular structured regular polysulfone honeycomb film where the sizes of pores were controlled by altering humidity, solution concentration, and molecular weight parameters and they reported that these films could be used for cell culture substrates but also for membranes since polysulfone is resistant to acids, detergents, hot water, and steam.²²² Saunders et al. fabricated porous polyethylene oxide-b-polyfluoro octylmethacrylate diblock copolymer films by drop casting of polymer in Freon (1,1,2-trichlorotrifluoroethane) solution onto oxidized silicon substrates. The increase in polymer hydrophobicity resulted in a reduction in the wettability of the air/Freon interface, which leads to a decrease in the nucleation of water droplets affecting the finalized pore size and

packing order in the polymer films. An increase in the nucleation density leads to smaller final droplet size and this is a promising way to produce porous films having various pore sizes and spacing.²²³ Liu and coworkers produced fluorescent honeycomb-patterned films of amphiphilic hyperbranched poly(amidoamine)s with high reproducibility on variety of substrates in a wide range of humidities. They reported that the patterned film thicknesses can be changed from nanometer to micrometer scale by altering the polymer concentration.²²⁴

Park and Kim used cellulose acetate butyrate in THF under humid conditions to obtain 2 distinct morphologies as top and bottom layers with higher and lower porosities by applying the spin-coating technique where the pattern was applied for broad-band antireflection coating.²²⁵ Park et al. also examined the effects of interfacial tension and polymer concentration on the porous structure of cellulose acetate butyrate films prepared by spin-coating technique using a THF and chloroform mixture under humid conditions. Final film morphologies have been attributed to the combination effects of speed of the solvent evaporation and interfacial energy between water droplets and the solvent. This strategy could be applied for manufacturing polymeric films having different porous structures and physical properties and has found an application area such as dielectric layers and thermal insulators with various capacitances.²²⁶ Orlov et al. fabricated microporous thin film membranes from solutions containing poly(2-vinylpyridine) partially quaternized with 1,4-diiodobutane, a pH responsive polymer, and spin coated them onto solid substrates in a controlled humid environment. They discussed the possible mechanism of pore formation and concluded that humidity is essential for the formation of pores. These membranes were cross-linked by temperature annealing and after cross-linking membranes demonstrated pH-dependent swelling, which makes them potentially attractive for size dependent filtering, drug delivery systems, and sensors.²²⁷ Munoz Bonilla et al. obtained breath figure patterns on functional surfaces by the surface segregation of a statistical glycopolymer, (S-co-2-(D-glucopyranosyl) aminocarbonyloxy ethyl acrylate). The blends of this copolymer and high-molecular-weight PS were spin coated from THF solutions and it was shown that blend composition and relative humidity play an important role in the size and distribution of the pores. The potential usages of these structures as templates were proposed for the attachment of bioactive molecules.²²⁸

7. Conclusions

The factors controlling drop condensation on a solid surface in air or in controlled conditions is an important topic and is now gaining a broader audience with the advent of nanotechnology and advanced biotechnology in the last 2 decades with a rapid increase of the number of publications in this field. Drop condensation on substrates plays a crucial role in many scientific applications such as heat transfer, water harvesting from the humid atmosphere, and hexagonal pattern formation on polymers using the breath figures method. In this review, we discussed the developments in water harvesting from dew using radiative cooling, or by the use of surfaces synthesized by bio-inspiration, and recent studies of drop condensation on superhydrophobic surfaces and on SAMs. We also reviewed the experimental, theoretical, and simulation studies on the growth of breath figures. Lastly, we discussed the topic of polymer templating (especially hexagonal pattern formation on polymers) using the breath figures method. This technique promises to grow in use in nanotechnology, biotechnology, and chemistry; however, only some parts of its mechanistic details are well understood despite the apparent simplicity of the process due to the presence of many process variables such as solvent, concentration, polymer type, molecular weight, relative humidity, temperature, and substrate type. Much research is needed on this topic in order to achieve good understanding and better industrial applications in fields such as photovoltaics, cell-growth media, scaffolding, refractive-index materials, superhydrophobic surfaces, catalysis, optics, filtration, and nano- and micro-reactors.

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