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One-step process to create porous structures in cross-linked polymer films via breath-figure formations during in situ cross-linking reactions

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ABSTRACT

This work demonstrates a new strategy of producing honeycomb-like porous structures in cross-linked polymer films via a simple one-step synthesis/fabrication process. This is based on the "breath figure" formation during the in situ cross-linking of reactive monomer solutions. A chloroform solution, containing tert-butyl acrylate monomer and tetraethylene glycol dimethacrylate cross-linker, was cross-linked upon UV radiation under a moist and nitrogen saturated chamber. Micron-sized pores with reasonable uniformity were obtained in the cross-linked polymer films. The size, shape, uniformity and ordering of the pores show significant dependences on the processing conditions. Using this method, porous structures were also achieved in a commercially available photo-active resin, NOA 65, illustrating the generality of this approach.

1. Introduction

Macro- or meso- porous films with highly ordered pore-structures have received much attention because of their potential applications in photonics [1], electronics [2], and biotechnologies [3]. Top-down lithographic techniques, such as photo-lithography [4] and contact lithography [5,6], can reliably fabricate micro- and nano-structures with high uniformity. However, they usually require multiple processing steps, expensive instruments, and pre-patterned templates or masks. In comparison, bottom-up fabrication approaches become increasingly attractive due to their simplicity, high throughput, and low fabrication cost, often by exploiting self-assembly mechanisms of colloidal particles [7–19], emulsions [20–22], and block copolymers [23–25].

Among them, "Breath Figure" (BF) is one of the most simple and elegant bottom-up assembly techniques to create ordered pores in polymeric films. BF method exploits the nucleation and assembly of water droplets, within an evaporating polymer solution, on solid surfaces under a humid environment. Briefly, the evaporation of the volatile solvent causes a local temperature drop (to below the dew point of water) in the concentrating polymer solution. In the presence of moisture, water will condense in such a cooler surface/film via a nucleation and growth process. As the remaining polymer solution continues to concentrate, the water droplets, separated by a layer of polymer, self-organize into well-ordered honeycomb morphology. Once the polymer solution evolves into a gel-like state, the honeycomb structure is then fixed. Finally, the polymer vitrifies completely, and a polymer film containing honeycomb pores is obtained after the removal of entrapped water droplets.

This "moist-casting" technique, first reported by Widawski et al. [26], has attracted broad interests and has been applied to create porous structures in different types of polymeric materials [27]. The conditions for BF formations highly depend on the material chosen and the underlying mechanisms for BF formation could be different [27]. Nevertheless, BF method is of significant interest for a range of potential applications due to its simplicity. Correspondingly, the class of materials that can be used as matrix for the BF formations are continuously expanding: from block copolymers or functionalized polymers [28–32], to biodegradable polymers [33], to organometals and functionalized metal nanoparticles [34–36] or ceramic materials [37].

Compared with their linear counterparts, cross-linked polymers have many advantages, particularly, their resistance against solvent dissolution and extended rubbery regions at high temperature. These make them attractive in applications such as shape memory polymers, dental resins, adhesives and tissue scaffolds. To date, cross-linked polymer films containing BF- templated porous structures were obtained by cross-linking the matrix after the BF

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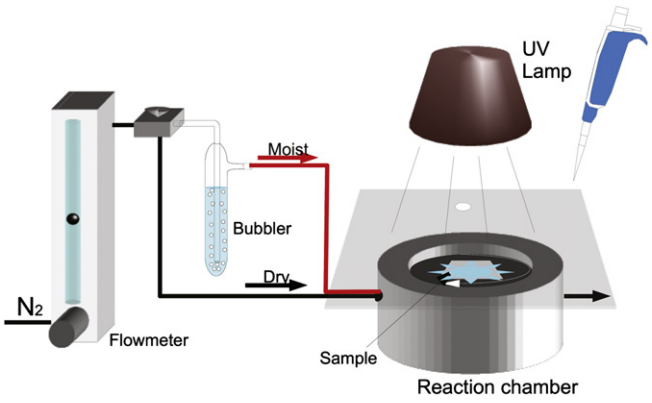

Fig. 1. Schematic of the experimental setup for the in-situ synthesis/fabrication strategy.

formations [38–40]. This synthesis/processing route requires that the BF-forming polymers contain cross-linkable chemical groups.

In this paper, we present a simple and convenient one-step method to create BF structures in cross-linked polymer films, by in situ polymerization of an evaporating monomer solution in the presence of moisture. Both an acrylate-based system and a commercially available reactive system demonstrated successful formation of porous structures via this technique.

2. Experimental

The monomer solution was prepared by mixing tert-butyl acrylate (TBA, 98%, Sigma Aldrich, used as received) and tetraethylene glycol dimethacrylate (TGDMA, 99%, Polysciences Inc. used as received) in a ratio of 80/20 w/w. Conventionally, the cross-linked bulk polymer based on this formulation shows great optical transparency and high biocompatibility, making them attractive for applications ranging from dental materials, to bio-sensor, and to biomedical devices [41–43]. The subsequent cross-linking of these monomers in this study were carried out by UV-induced free radical polymerization, with 0.2% w/w 2,2-dimethoxy-2-phenyl-acetophenone (99%, Aldrich) as the photo initiator. The reactive monomer mixtures were dissolved in chloroform (spectroscopic grade, Sigma Aldrich, used as received) with volume fraction ranging from 5% to 30% v/v and mixed by means of a vortex mixer until complete dissolution. In addition to above acrylate-based reactive system, a commercially formulated optical resin, NOA 65® (distributed by the Norland Products Incorporated Company), was also used for this study. This resin consists of mercapto-ester with acrylate monomer [44]. For this system, CS_2 was adopted as the solvent for the BF formation, with a NOA concentration of 10% by weight.

The in-situ cross-linking of both systems during the BF formation was initiated with a long wave Ultraviolet lamp (Black-Ray, B-100AP), which was set at ca 5 cm from the sample surface. The UV energy density at the surface of the samples was 6 mW/cm^2, determined by a radiometer. The total UV exposure was set to 15 min for the acrylate-based system to ensure the complete evaporation of the solvent and cross-link of the monomers. In comparison, only 3 min UV exposure was used for NOA samples because of its faster reaction rate.

The process was carried out in a home–built reaction chamber (Fig. 1), designed to meet all the requirements for both the free-radical polymerization and BF formation. The chamber consists of a closed aluminum box containing a gas inlet and outlet, with a 2 mm-thick glass cover on the top. The glass cover contains a small hole to allow the injection of the monomer solution and can then slide to fully cover the chamber. N_2 was used to purge out most of the oxygen, which is known to be detrimental for the free radical polymerization of the acrylate-based system. In comparison, the cross-linking of NOA 65 is much more oxygen-tolerant. The flow of gas was controlled by a flow-meter and a three-way valve which allows purging N_2 either directly into the chamber or through a gas bubbler (to saturate with water vapor) before entering the chamber. Such design allows selectively purging dry or moist N_2 into the chamber during the UV exposure. Correspondingly, N_2 flow rates between 0.8 and 1.6 l/min were used for the acrylate-based system and 5 l/min for the NOA/CS_2 system. To help planarizing the evaporating/cross-linking solution, a low-profile rotating fan was mounted at the bottom of the chamber, whose speed was controlled by varying the supplying voltage (between 3 and 5 V).

The obtained porous samples, after removing the entrapped water droplets, were characterized with SEM (Zeiss, Supra 60). The acquired SEM images were then analyzed using Image J, (National Institutes of Health, USA). Geometric parameters of the porous films, including perimeter, diameter, circularity, and surface coverage of the pores, and wall thickness between the pores, as well as FFT analysis were performed with Image J on converted binary images with 2000 × or 1500 × magnification. Specifically, the circularity of the pores was calculated according to, circularity $= 4\pi(\text{area}/\text{perimeter}^2)$ and equals 1, 0.907, and 0.785 in the case of a circle, hexagon, and square, respectively. Wall thickness was calculated from averaging at least 100 measurements.

3. Results and discussion

Before describing the detailed experimental findings, we note that the chemical and physical processes that involved in this one-step method are extremely complicated: evaporation of solvent, polymerization and cross-linking between the monomers and cross-linkers, as well as condensations and rearrangements of the water droplets. For such a highly non-equilibrium process, the final BF morphology is expected to depend strongly on the following processing parameters: moist flow rate, UV radiation intensity, concentration and formulation of the monomers, evaporation speed of the solvent, and wettability of the solution on the solid substrates. Furthermore, these factors are highly interrelated, i.e. altering one would result in significant variations of others. In this report, we primarily focus on the proof-of-concept of this approach, by demonstrating the successful fabrication of the porous films, and examining the role of few basic processing parameters.

Table 1
Processing parameters for the reactive systems.

	Sample	Flow rate, l/min	Initial spin, 2 s	Pre-polymerization under dry N_2, min	Polymerization under moist N_2, min	Post-polymerization under dry N_2, min
Acrylate-based	A	1.6	√	–	15	–
	B	1.6	√	2	13	–
	C	1.6	√	–	1	14
	D	0.8	√	–	2	14
NOA 65	E	5	–	–	3	–