Progress in Polymer Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Review

Towards hierarchically ordered functional porous polymeric surfaces prepared by the breath figures approach

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ARTICLE INFO

Article history:
Received 15 February 2012
Received in revised form 31 July 2013
Accepted 2 August 2013
Available online xxx

Keywords:
Breath figures
Polymer nanostructures
Morphology
Hierarchical
Functional
Stimuli-responsive

ABSTRACT

This article reviews the approaches developed to prepare and characterize porous structured materials by using the breath figures (BF) methodology. In particular, we have analyzed the topographical modifications of the surface that can be tuned with this approach, such as the control of the pore characteristics, changes in the pore morphology or use of non-planar substrates to create the porous materials among others. We have also given special attention to the functionality inside of the pores and how this can be created by using different kinds of polymers, from homopolymers to hybrid materials, as well as by changing the pore functionally after chemical modification. The approaches followed to obtain hierarchical structures, for example, by combination of the BF approach and nanostructure formation within the pores or by using soft-lithography have also been examined. In addition, we discuss the feasibility of obtaining stimuli-responsive honeycomb structured surfaces. The potential applications in different areas such as biomedicine, optics and so on, are also pointed out. Finally, we comment on some future perspectives of breath figures approach.

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http://dx.doi.org/10.1016/j.progpolymsci.2013.08.006

1. Introduction

The creation of porous polymer surfaces is a center of interest in current research. Porous surfaces possess extremely high specific surface areas, thus allowing their employment in a large variety of applications including electronics, photonics or biotechnology [1,2]. Pore size and distribution can play a major role in selective transportation or in insulation processes among others [3]. Those porous materials with cavities in the micrometer size range are interesting in catalysis, sensors, membrane preparation or as scaffolds for composite materials. More precisely porous materials with pore dimensions comparable to the wavelength of visible light are of interest as photonic bandgaps and optical stop-bands.

Structures with micrometer or submicrometer dimensions can be created using different templating methods [4,5]. A wide variety of approaches have been developed and employed to prepare microporous structured materials, including the use of templates such as ordered arrays of colloidal particles to produce inverse opal structures [6–9], from transformed polymeric sphere arrays [10,11], using emulsion droplets as templates [12], employing natural biological templates [13–16], by phase inversion [17], self-organized surfactants [18], microphase separated or electric-field-induced block copolymers patterning [19–21], etc. Other alternatives include direct writing of polymer patterns [22], the use of photo- or electrochemically polymerizable precursors [23] or soft lithographic methods [24].

Nevertheless, the templates that are required in most of the previously mentioned methods must be removed after the fabrication of the porous films and in most of the cases they are not easily prepared or eliminated. An alternative approach is the use of breath figures (BF) templating methods, in which the template consists of an ordered array of water droplets that may be removed by simple evaporation. The breath figures technique is one of the most widely employed methods for the fabrication of porous polymer films [25,26]. Several significant advantages justify its extensive use. First, the self-removal of the template favors a reduction on the production time and costs. Second, BF allows the employment of a wide variety of materials ranging from polymers to hybrid nanocomposites, thus leading to porous films with diverse properties. Finally, as will be analyzed throughout this review, the external parameters (temperature, air humidity, ...) and those related with the preparation procedure (solvent, polymer concentration, ...) are directly related to the pore dimensions and shape obtained. Thus, the pore sizes may be manipulated by controlling these parameters.

Reviews concerning the preparation of porous materials by the breath figures approach written several years ago, such as the extensive review elaborated by Bunz [27], do not include the most recent literature and others more recently published have each been limited to particular aspects on this topic [5,28,29]. By contrast, the objective here is to give a complete and exhaustive review on the state of the art and the future on the preparation of porous structures based on the breath figures mechanism, presenting detailed information on the principal aspects of pore and structure formation. Two sections are devoted to the preparation of more sophisticated materials involving stimuli-responsive structures and hierarchically ordered materials. The preparation of pores with adaptive behavior may facilitate applications to systems that require antagonist behavior depending on the environmental conditions. Furthermore, hierarchically ordered systems have evidenced improved performance compared to systems ordered on one length scale.

In spite of scarce examples involving the increase of complexity in the pore design, this review includes the most recent literature. For that purpose, this manuscript is divided into 6 main parts involving the following aspects. The main mechanistic characteristics of this process to further analyze the key parameters that control the formation of the pores will be described in Section 2. An overview of the principal strategies followed to produce pores with different sizes and shapes and the means to modify the chemical composition of the pore interface will be given in Section 3. Up to now, the control of the surface topography and surface chemical composition has been accomplished

Please cite this article in press as: Muñoz-Bonilla A, et al. Towards hierarchically ordered functional porous polymeric surfaces prepared by the breath figures approach. Prog Polym Sci (2013), http://dx.doi.org/10.1016/j.progpolymsci.2013.08.006