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Dendritic amphiphiles as additives for honeycomb-like patterned surfaces by breath figures: Role of the molecular characteristics on the pore morphology

A.S. De León [a], S. Malhotra [b], M. Molina [b], R. Haag [b], M. Calderón [b,*], J. Rodríguez-Hernández [a], A. Muñoz-Bonilla [c,*]

[a] Instituto de Ciencia y Tecnología de Polímeros (ICTP), Consejo Superior de Investigaciones Científicas (CSIC), C/Juan de la Cierva 3, 28006 Madrid, Spain
[b] Freie Universität Berlin, Institute of Chemistry and Biochemistry, Takustr. 3, 14195 Berlin, Germany
[c] Departamento de Química-Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, C/Francisco Tomás y Valiente 7, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

The current study presents a library of honeycomb-like patterned surfaces developed from a variety of different water-soluble amphiphilic dendrons. When compared to commercial surfactants, the dendrons produce a wide variety of porous surfaces due to their well-defined branched structure. Different functionalities and generations of dendrons have been studied. A singular hierarchical distribution of the dendrons, forming small nanoparticles (micelles) only at the inner edges of the holes (coffee stain effect) is observed. Once the surfaces are fabricated, these dendrons can be easily recovered via simple aqueous washing. After this treatment, the surfaces exhibit a high hydrophobic character (up to 140°) due to the high porosity. This behavior can be described by the Cassie–Baxter model.

1. Introduction

The preparation of porous polymeric materials with pores ranging from micrometer to nanometer scale had been achieved following different approaches, including the use of templates such as ordered arrays of colloidal particles to produce inverse opal structures [1–4], emulsion droplets [5], sphere arrays [6,7], employing natural biological templates [8–10], self-organized surfactants [11], and by phase inversion [12]. Other alternatives include direct writing of polymer patterns [13], the use of photo- or electrochemically polymerizable precursors [14] or soft lithographic methods [15].

In addition to the methodologies mentioned above, the breath figures technique is among the most extended approaches. One key advantage of this approach is its versatility. By using this methodology, porous surfaces with variable dimensions (nanometer to micrometer scale), shapes (round, elliptical, rectangular) [16], and also chemical functionalities inside and outside the pores have been developed [17,18]. Moreover, in contrast to the above mentioned methodologies porous films fabricated by this approach do not require the use of templates that are difficult to remove completely. The resulting porous materials have wide spread applications in the areas of electronics, photonics, biotechnology, etc. [19–21].

Experimentally, the preparation of porous films by the breath figures approach typically resorts to a simple evaporation of a volatile polymer solution in a humid atmosphere. During the evaporation of the solvent the temperature of the solution surface decreases, thus causing condensation of water as small droplets on the surface. Then the water droplets can grow and be ordered in a honeycomb structure, resulting in a porous polymeric film after complete solvent and water evaporation. Factors like humidity, temperature, polymer concentration, as well as the topological and functional characteristics of the polymer employed, control the morphology and distribution of the pores obtained to a large extent [18].

* Corresponding authors.
E-mail addresses: marcelo.calderon@fu-berlin.de (M. Calderón), alexandra.munnoz@uam.es (A. Muñoz-Bonilla).

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Concerning the macromolecular parameters, several studies revealed that branched structures appear to stabilize the condensed water droplets and favor the formation of ordered porous interfaces. This is, for instance, the case of the use of star polymers instead of their linear homologues [22]. Non-linear architectures employed either as unique material or as additive include grafted polymers [23] or microgels [24].

Dendritic structures which are formed by well-defined branched structures in the nanometric scale are particularly interesting to decorate porous films. Amongst other applications, they can be used as building blocks or nanospacer arms in order to obtain complex materials [25]. Also, due to their ability to form core–shell nanoparticles they have interesting applications in the biomedical fields, such as tissue engineering or gene delivery [26–28]. They have also been used as a modifying agent in surfaces due to their possibility of tuning the hydrophilicity, adhesion, and solubility by controlling the number of arms, branches as well as the chemical composition of the dendritic architecture used [29]. The hydrophilic character of the polymer employed also enhances the water condensation and tends to condense larger droplets forming thus larger pores. Few systems allow the incorporation of branching units and hydrophilic moieties. For instance, Chang et al. studied the effect of grafting dendrimeric structures onto polystyrene and polyurethane systems [30]. However, most of them were obtained by polymerization and therefore, polydisperse materials were obtained. Moreover, these branched structures have been employed as unique component in the formation of breath figures [31].

Amphiphilic, low molecular weight (LMW) dendritic architectures (e.g., dendrons) with hydrophobic portions at the focal point, which form self-assembled multivalent systems (termed self-assembling dendrimers or pseudodendrimers) in aqueous media were successfully synthesized and evaluated for their aggregation and potential biomedical applications [32–36]. Recently, employing olygoglycerol (OG) dendrons, our research group has successfully shown that such an approach can well augment multivalent interactions for drug, gene and other bioactives which leads to highly interesting effects if both multifunctional dendrons and hydrophobic alkyl chains are combined [37–40]. OG-based dendrons serving as the hydrophilic part in a given amphiphile are based on the very biocompatible glycerol building block with a tree-like structure and a large number of hydroxyl groups. Their water solubility, physiological safety, and post hydroxyl modifications offer excellent opportunities for multivalent interactions with biological substrates. Additionally, the degree of branching motifs and thus flexibility can be varied by choosing a certain dendron generation [41–43].

Herein, we present the use of two families of monodisperse and defined OG-based dendritic structures having different generations (G1 and G2) and either hydroxyl or amine terminal groups, as additives to prepare porous films. The role of the hydrophilicity and the chemical structure of the additives, as well as the blend composition on the final surface morphology have been described. Moreover, we explored two unique characteristics of these materials. On one hand, the particular distribution of the additive within the pore which leads to the coffee stain effect and on the other hand the possibility to remove the dendritic additive to produce highly hydrophobic porous surfaces were both investigated. The recovered additive could be reused again to generate further new templates. The present study elucidates the use of defined, low molecular weight, monodispersed dendritic nano architectures for developing highly hydrophobic porous films. The possibility of recycling the dendrons would permit us to develop a continuous system of films fabrication with potential applications in various fields of nanoscience.

2. Experimental

2.1. Materials

High molecular weight polystyrene (PS, Aldrich, $M_w = 3 \cdot 10^5$ g mol^{-1}) was used as polymeric matrix. Fluorescein isothiocyanate (FITC, 98%) and commercial surfactant Brij® L4 were purchased from Aldrich. Dendrons $\mathbf{d_1}$, $\mathbf{d_2}$, and $\mathbf{d_3}$ were synthesized according to the previously reported procedures [38–40,44]. Chloroform ($CHCl_3$) was supplied by Scharlau and round glass coverslips of 12 mm diameter were obtained from Ted Pella Inc.

2.2. Films preparation of the porous films by the breath figures technique

Different blends were studied by varying the concentration of dendritic structures and Brij L4 surfactant from 0.1 mg mL^{-1} to 10.0 mg mL^{-1} (0.11–40.00 wt%) whereas the concentration of PS matrix ranged from 15.0 to 90.0 mg mL^{-1}. $CHCl_3$ was used as solvent in all the cases. The chemical compositions of all prepared blends are summarized in Table 1. Films were obtained from these chloroform solutions by casting onto glass wafers under high controlled humidity (relative humidity (RH) = 80%) inside of a closed chamber at room temperature.

2.3. Recovery of the dendrons

Upon film formation using the amphiphilic dendrons, these could be removed from the interface. For that purpose, the surfaces were washed with 10 mL of milliQ water for less than 1 min. Then, the water solution was freeze-dried and lyophilized in order to recover the dendrons. The obtained solid was characterized by ^{1}H NMR and the percentage of recovery was determined by mass difference, obtaining in all the cases a recovery rate of at least 60 wt%.

2.4. Characterization

^{1}H NMR analysis was performed in a Bruker 700 MHz NMR spectrometer using deuterated water as solvent. Scanning electron microscopy (SEM) measurements were obtained using either a field emission scanning electron microscope (FE-SEM) (Hitachi, SU 8000, Japan) at 10.0 kV in secondary electron imaging mode or a Philips XL30 with an acceleration voltage of 25 kV. The samples were coated with gold–palladium (80/20) prior to scanning. Data processing of the images was done using ImageJ software. Roughness of the surfaces were quantified with the f parameter of the Cassie–Baxter equation, described as the fraction of the projected wet area [45]. Static contact angles measurements were performed by using a contact angle goniometer (Data Physics Instruments, Germany) with the sessile drop method. Cassie–Baxter state model was studied according to the following equation:

$$\cos\theta_{CB} = f \cdot (\cos\theta_i + 1) - 1 \quad (1)$$

Table 1
Weight percentage (wt%) values of the additive (dendritic structures or Brij L4 surfactant) in the blends prepared by varying both the additive and the PS concentration in the chloroform solution.

Additive concentration (mg mL^{-1})	PS concentration (mg mL^{-1})				
	15	30	45	60	90
0.1	0.66	0.33	0.22	0.17	0.11
0.5	3.22	1.64	1.10	0.83	0.55
1.0	6.25	3.22	2.17	1.64	1.10
10.0	40.00	25.00	18.18	14.28	10.00