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Self-Functionalizing Polymer Film Surfaces Assisted by Specific Polystyrene End-Tagging

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Two simple approaches to build up micropatterned functionalized polymer films are reported here. Both of them are based on the formation of porous films consisting of two-dimensionally ordered void structures, produced by evaporation of a polymer solution in the presence of humidity. In the first approach, we utilize an amino-terminated linear polystyrene to fabricate honeycomb structured films in which the cavities are enriched with amino groups that preserve their chemical reactivity. This allows, in principle, to obtain films with different surface functionality by simply changing the chain-end of the polymer used. In the second approach, we synthesize a luminescent chain-ended polystyrene to show how the honeycomb structures can be easily transformed, by a thermal treatment, into flat micropatterned fluorescent films. Both the microporous and the flat micropatterned films resulting from this study are attractive materials since the chemical functions distributed on their surface can further react with other molecules to provide a more complex array suitable for biological tests.

Introduction

In nature, specific functionalities of organisms are often regulated by the precise micro or nanostructures on their surfaces, more than by intrinsic properties of the materials. In a similar way, the control over surface morphology is an essential goal for those researchers that aim at the manipulation and construction of new functional materials.[1−6] Indeed the possibility of obtaining in the laboratory materials having not only definite surface morphology but also even a controlled distribution of chemical functionalities is a challenge that represents a fascinating field of research, one that could possibly lead to applications in different areas like microelectronics, microoptics, biotechnology, and smart packaging.[7−11] These features are commonly achieved by top-down strategies such as microcontact printing or photolithographic techniques combined with one or more functionalization steps. Although multistep approaches are highly versatile and normally ensure accurate results, self-organization techniques have the undisputable advantages of being fast, simple, and cheap.

In this view, the water drop templating method known as the Breath Figure (BF) imprinting procedure comprises a promising method for the preparation of polymer films with a regular distribution of cavities on their surface. This technique is based on the evaporative cooling of a polymer solution in a wet environment, allowing water droplets to produce ordered arrays of pores on the film surface.[12] When the process is adequately controlled, several parameters can be adjusted (solvent, polymer concentration, evaporation rate, humidity) to obtain different film morphologies. In particular, patterned structures with regular size pores ranging from 200 nm to 10 μm can be obtained, mono- and multilayers can be formed, as well as deformation of the spherical cavities can be achieved.[13−15] Different models have been proposed to explain BF patterns formation involving thermocapillary forces, Bérnard−Marangoni

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convection, and surface tension effects.[13,16−18] Our group previously described this phenomenon in detail.[19] It was pointed out how the presence of hydrophilic terminal groups in linear polystyrenes promotes the stabilization of the polymer−water interface during the BF formation, thus increasing the regularity of the honeycomb structures. Moreover we evidenced using the ToF-SIMS (time-of-flight secondary-ion mass spectrometry) technique how these polar groups concentrate inside the film cavities.[20] A similar behavior, observed by several authors, is explained considering that water droplets act not only as template for holes array but also can orient polar functions inside the cavities.[18,21−24]

In this work we focus our attention on two different approaches to build up micropatterned functionalized films using the BF technique. In the first one we use an amino-terminated polystyrene (PS) to produce thin porous films having the cavities enriched in -NH_2 residues. Cavities are then selectively "painted" with a specific fluorescent dye. In the second approach we utilize a fluorescent labeled amino-polystyrene to show how the honeycomb structures can easily be transformed into flat micropatterned fluorescent films.

Experimental Section

Materials. Tetrahydrofuran (THF) (Riedel de Haën) was distilled from Na/K alloy before use. Styrene (Aldrich) was purified through the trap-by-trap technique before use. 2,2,6,6-Tetramethyl-1-piperidyloxy radical (TEMPO) derivatives (4-amino-TEMPO, 4-hydroxy-TEMPO, and 4-carboxy-TEMPO), as well as all other reagents and solvents mentioned in this section, were purchased from Sigma-Aldrich and used without further purification.

GPC measurements were carried out on a Waters SEC system equipped with a 2414 RI and a 490 UV detectors, 2 PL gel Mix C columns, THF as solvent, and PS as reference.

Confocal and fluorescence images were collected with a Nikon Eclipse TE2000-U inverted confocal microscope with a long working distance and using a Plan Fluor objective (magnification 40, N.A. 0.75). The confocal measurements were done with an Ar^+−ion laser at 488 nm.

Atomic force microscopy (AFM) investigations were performed using a NT-MDT NTEGRA apparatus in tapping mode under ambient conditions.

Scanning Electron Microscopy images were recorded using a Zeiss Leo 982 apparatus at 3 kV tension.

Synthesis of Boron-Dipyrromethene TEMPO Derivative (TEMPO-NH-bodipy) (6). *Compound 3*. 3-Ethyl-2,4-dimethyl-1*H*-pyrrole **1** (0.80 cm^3, 5.94 mmol) and 4-[3-(1,3-dioxoisoindolin-2-yl)propoxy]benzaldehyde **2** (920 mg, 2.97 mmol) were dissolved in dry CH_2Cl_2 (180 cm^3) under nitrogen atmosphere. One drop of trifluoroacetic acid was added, and the resulting mixture was stirred at room temperature for 1 h. The solution was diluted with CH_2Cl_2 (90 cm^3), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (1.35 g, 5.94 mmol) was added. Stirring was continued for 1 h, followed by the addition of DIPEA (7.40 cm^3, 44.55 mmol) and $BF_3 \cdot Et_2O$ (7.50 cm^3, 59.40 mmol). After 1 h the reaction mixture was treated with water (300 cm^3), and the two-phases mixture was passed through a Celite filter. The organic phase was separated and washed again with water (2 × 150 cm^3), dried over Na_2SO_4, and evaporated to dryness. The dark brown residue was purified by silica gel column chromatography using dichloromethane as eluent to give **3** (810 mg, 47%) as an red-orange solid. δ_H(400 MHz; $CDCl_3$) 7.85 (2 H, m), 7.73 (2 H, m), 7.11 (2 H, d, *J* 8.4), 6.88 (2 H, d, *J* 8.4), 4.11 (2 H, t, *J* 6.4), 3.96 (2 H, t, *J* 6.4), 2.53 (6 H, s), 2.27 (6 H, m), 1.32 (6 H, s), 0.98 (6 H, t, *J* 7.5); δ_C(100 MHz; $CDCl_3$) 168.4, 159.1, 153.5, 140.3, 138.5, 134.0, 132.6, 132.2, 131.2, 129.4, 128.0, 123.3, 114.9, 65.9, 35.5, 28.3, 17.1, 14.6, 12.5, 11.9. Anal. Calcd (%) for $C_{34}H_{36}BF_2N_3O_3$ C 69.99, H 6.22, N 7.20; Found C 70.12, H 6.17, N 7.14.

Compound 4. Hydrazine monohydrate (0.6 cm^3, 12.34 mmol) was added to a solution of **3** (150 mg, 0.26 mmol) in EtOH (20 cm^3), and the resulting mixture was stirred at reflux, monitoring the disappearance of starting compound by TLC (silica, CH_2Cl_2). The reaction mixture was then cooled at room temperature, and a white solid was filtered off. The deep red solution was evaporated to dryness, and the obtained residue was purified by silica gel column chromatography using chloroform/methanol as eluent (9:1) to give **4** (950 mg, 82%) as a red solid. δ_H(400 MHz; $CDCl_3$) 7.16 (2 H, d, *J* 8.4), 7.01 (2 H, d, *J* 8.4), 4.14 (2 H, t, *J* 6.4), 3.06 (2 H, t, *J* 6.4), 2.09 (2 H, s. all.), 2.53 (6 H, s), 2.30 (4 H, quartet, *J* 7.6), 2.08 (2 H, quintet, *J* 6.4), 1.33 (6 H, s), 0.98 (6 H, t, *J* 7.6); δ_C(100 MHz; $CDCl_3$) 159.2, 153.5, 140.2, 138.4, 132.7, 131.2, 129.5, 128.1, 116.1, 114.9, 65.9, 38.9, 31.5, 29.7, 17.1, 14.6, 12.5, 11.9. Anal. Calcd (%) for $C_{26}H_{34}BF_2N_3O$ C 68.88, H 7.56, N 9.27; Found C 68.35, H 7.61, N 9.35.

Compound 5. Compound **4** (130 mg, 0.29 mmol) was dissolved in dry toluene (20 cm^3) and Et_3N (0.37 cm^3, 2.87 mmol) under a nitrogen atmosphere. Then thiophosgene (0.065 cm^3, 0.86 mmol) was added to the solution, and the mixture was refluxed under nitrogen until thin-layer chromatography (TLC) showed complete consumption of the starting material (silica, EtP/CH_2Cl_2 4:1). Then the clean solution was evaporate to dryness to afford a brown residue, which was purified by silica gel column chromatography using petroleum ether/dichloromethane as eluent (1:1) to give **5** (113 mg, 80%) as a red powder. δ_H(400 MHz; $CDCl_3$) 7.18 (2 H, d, *J* 8.4), 7.01 (2 H, d, *J* 8.4), 4.16 (2 H, t, *J* 5.6), 3.83 (2 H, t, *J* 6.0), 2.53 (6 H, s), 2.31 (4 H, quartet, *J* 7.6), 2.22 (2 H, quintet, *J* 5.6), 1.34 (6 H, s), 0.99 (6 H, t, *J* 7.6); δ_C(100 MHz; $CDCl_3$) 158.9, 153.6, 140.0, 138.4, 132.7, 131.2, 129.6, 128.4, 115.0, 64.1, 42.1, 29.9, 17.1, 14.7, 12.5, 11.9. Anal. Calcd (%) for $C_{27}H_{32}BF_2N_3OS$ C 65.46, H 6.51, N 8.48; Found C 66.03, H 6.57, N 8.41.

Compound 6. A solution of 4-amino-TEMPO (31 mg, 0.18 mmol) in dry toluene (3 cm^3) was added dropwise to a solution of **5** (100 mg, 0.22 mmol) in dry toluene (6 cm^3) under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 5 h. After cooling, the organic solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography using toluene/ethyl acetate (1:1) as eluent, to afford **6** (50 mg, 42%) as a dark red solid. *m*/*z* (ESI)

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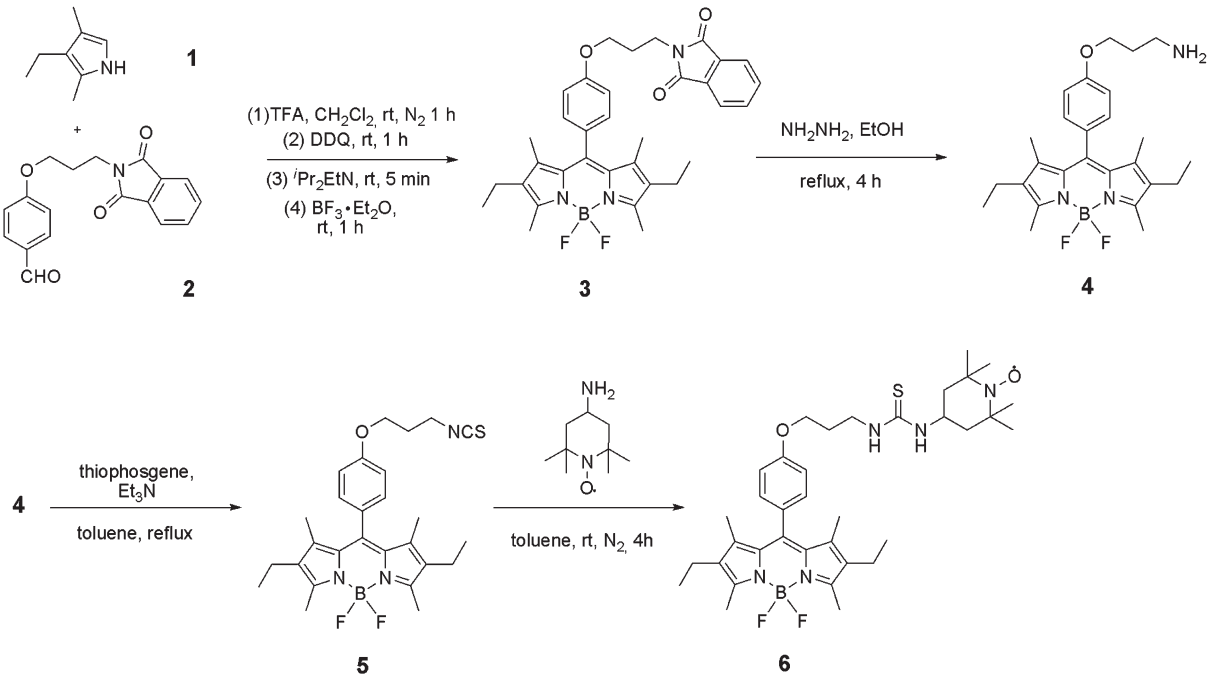
Scheme 1. Synthesis of TEMPO-NH-bodipy (6)



689.37070 ($M+Na^+$) $C_{36}H_{51}BF_2N_5OS$ requires 666.38. Anal. Calcd (%) for $C_{36}H_{51}BF_2N_5O_2S$ C 64.85, H 7.71, N 10.50; Found C 65.32, H 7.77, N 10.41.

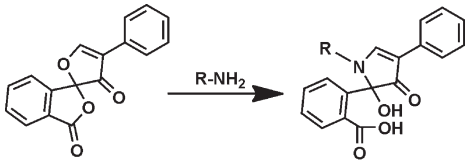
TEMPO Mediated Free Radical Polymerization of Styrene (General Procedure). In a Schlenk flask 0.040 mmol of TEMPO initiator were dissolved in 2 mL of styrene, flushed with nitrogen, and polymerized at 125 °C under vigorous stirring for expected times. After the polymerization was stopped, the cooled mixture was solubilized in small amounts of THF and then poured dropwise into methanol (150 mL) under stirring. The resulting precipitate was filtered and washed with fresh methanol. 4-Amino-TEMPO gave PST-NH_2 (GPC: M_w 9.38 kDa, M_w/M_n 1.8). 4-Carboxy-TEMPO gave PST-COOH (M_w 3.30 kDa, M_w/M_n 1.14). 4-Hydroxy-TEMPO gave PST-OH (GPC: M_w 5.15 kDa, M_w/M_n 1.2). TEMPO-NH-bodipy (**6**) gave PST-NH-bodipy (M_w 84.7 kDa, M_w/M_n 1.7).

Preparation of Samples. Microporous films were prepared by casting a CS_2 solution of the polymer on a glass microscopy slide or on a silicon wafer under a flow of moist nitrogen (60% R.H. at 25 °C), obtained by flowing nitrogen through a two-necked flask filled with water, at room temperature, at 2 L min^{-1} rate, respectively. Best results were obtained using a concentration of 1 mg mL^{-1} for all polymers except for PST-NH-bodipy, for which 4 mg mL^{-1} has been used. Thermal treatments were carried out by keeping the sample slide at 135 °C for 2 h under nitrogen, then slow cooling (1 °C/min) to room temperature. For fluorescence revelation of amino groups, the BF films of PST-NH_2 were dipped in a 4 mM fluorescamine solution (3:1 methanol/water v/v) at room temperature for 1 h, then dried at 50 °C for 2 h.

Results and Discussion

During the BF formation the condensation of water droplets at the air/polymer solution interface allows superficial polymer chains to orientate themselves by interaction of the polar terminal groups with the water droplets, so that porous films enriched with polar groups in the pores are achievable in principle. We have already shown how

Scheme 2. Reaction of Fluorescamine with Amines to Form a Fluorescent Compound



ToF-SIMS is a remarkably suitable technique to study the distribution of different chemical groups inside and outside the cavities of a honeycomb structured film prepared by the BF procedure.[20] In that study we used Tof-SIMS to characterize microporous films prepared using a TEMPO terminated PS in which piperydinyloxyl group was further converted into a more polar *p*-toluensulfonate acid salt. Here we have been able to demonstrate that even the less polar amino group is hydrophilic enough to produce PS porous films in which cavities are effectively enriched with -NH_2 groups. With this aim, an amino terminated PS (PST-NH_2) has been synthesized by nitroxide-mediated living radical polymerization,[25,26] and its carbon disulfide solution has been used to prepare thin films by the BF procedure. For a preliminary fast assay, these films have been treated with fluorescamine (Scheme 2), a common reagent for amino acid revelation. Fluorescamine is not fluorescent itself, but reacts with primary amine groups giving a highly fluorescent adduct.[27] This feature avoids undesirable fluorescent background phenomena.

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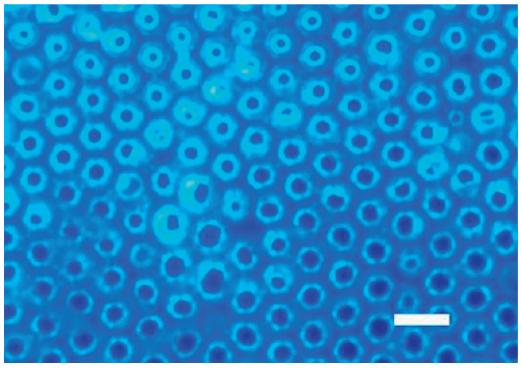

Figure 1. Fluorescence microscopy image of a PST-NH_2 honeycomb structured film after treatment with fluorescamine (scale bar is 5 μm long).

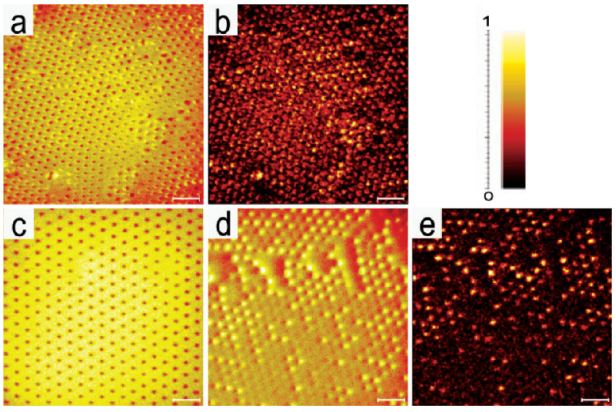

Figure 2. Negative ToF-SIMS images (scale bars are 10 μm long). a-b) PST-NH_2 microporous film: (a) sum of all anions; (b) m/z: 26 (CN^-). (c−e) PST-NH-bodipy microporous film: (c) sum of all anions before thermal treatment; (d) sum of all anions after 2 h of thermal treatment at 135 °C; (e) same film, m/z: 19 (F^-).

The fluorescence microscopy image of PST-NH_2 films after this treatment, shown in Figure 1, evidences that fluorescence response is higher inside the cavities, thus indicating an elevated concentration of reactive amino groups in those sites.

This result has been confirmed by ToF-SIMS analysis of an analogous film (Figure 2-a/b). Negative ion images show a large amount of CN^- ions, related to PS amino residues (i.e., TEMPO initiator) coming from the cavities. The imaging of the NH^- ion would have been more characteristic of the amino function but unfortunately Tof-SIMS sensitivity toward this ion is too weak to give a sufficiently contrasted image.

This enrichment of the cavity internal wall of the BF films with polymer chain end-groups, already reported in the literature,[14,21−23,28,29] transforms the perspectives of the BF approach from a mere building technique to a powerful procedure able to functionalize detailed areas of a polymeric surface with specific chemical groups. Similar results are also achievable with −OH and −COOH terminated linear PSs, which suggests that using this approach as an effective control over the chemical

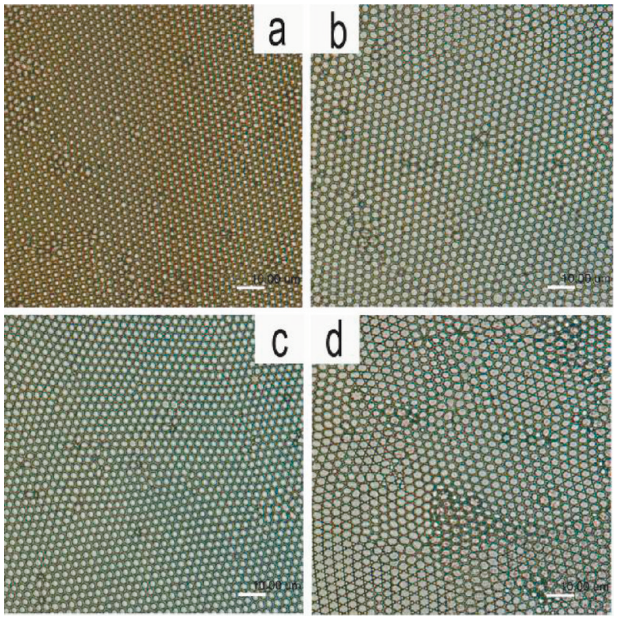

Figure 3. Micrographs of thin films prepared by casting 1 mg mL^{-1} CS_2 solutions of (a) PST-NH_2, (b) PST-COOH, (c) PST−OH, (d) PS-PAMS (scale bar is 10 μm long).

distribution, together with a precise surface morphology, is really possible. In fact, most of chemical functionalities are reactive toward one of these three chemical groups, which offers the possibility of anchoring bigger chemical fragments, such as biomolecules, to specific surface sites. To increase the amino group concentration inside the cavities, we have also synthesized a linear aminomethyl-polystyrene (PS-PAMS) starting from a commercially available PS. Unfortunately the decrease of amphiphilicity along the PS chain led to loss of regularity of the hexagonal pattern. (Figure 3-d).

Once the goal of functionalizing the inside of the pores with different chemical groups starting from a single material has been reached, a derivative of boron-dipyrromethene (bodipy)[30] has been synthesized and linked to the amino-TEMPO initiator to prepare a fluorescent labeled PS. As reported in Scheme 1, the bodipy derivative **3** has been prepared in 47% yield by condensation of 2 equiv of 3-ethyl-2,4-dimethylpyrrole **1** and aldehyde **2**[31,32] in the presence of TFA and DDQ, followed by the addition of $BF_3 \cdot OEt_2$. The deprotection of the phtalimido group has been readily performed by using hydrazine monohydrate in refluxing ethanol, affording derivative **4** in 82% yield. The amino group was converted into isothiocianate by reaction with thiophosgene in refluxing toluene and Et_3N as base, giving compound **5** in 80% yield. Finally the addition of **5** to 4-amino-TEMPO, carried out in toluene at room temperature, afforded luminescent labeled radical **6** in 42% yield. This modified TEMPO radical was employed as initiator for the living radical polymerization of styrene. The intense and narrow emission peak of bodipy centered at 540 nm

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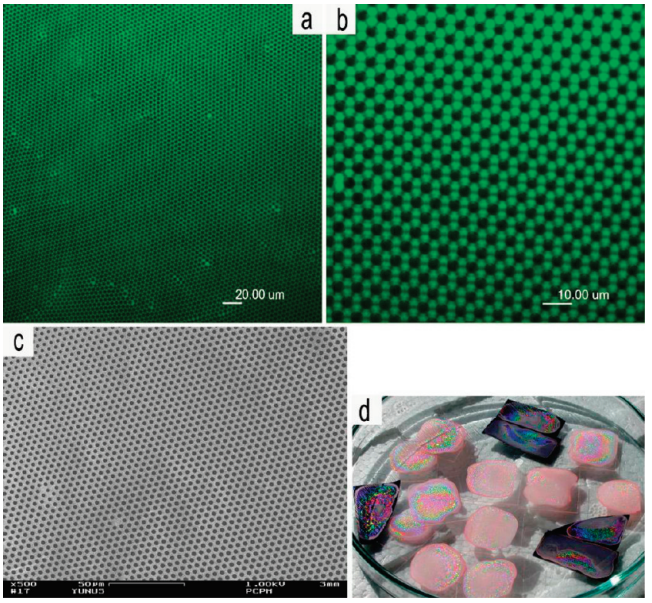

Figure 4. (a) PST-NH-bodipy honeycomb structured film; 330 μm^2 fluorescence microscopy image with few defects. (b) Bigger magnification of the same film. (c) SEM micrograph of same kind of film. (d) Films prepared by drop-casting a CS_2 solution of PST-NH-bodipy on glass microscopy coverslips and on silicon wafers.

makes the thin films obtained from this polymer suitable to be studied by fluorescence microscopy techniques. By casting a solution of this polymer under BF conditions, highly ordered porous films are easily obtained (Figure 4).

In these films, relatively wide areas (up to 0.5−0.6 mm^2) with none or few defects of the hexagonal order are achievable. Along these areas the diameter size distribution of pores is quite homogeneous, while for longer distances, a variation of ~40% has been recorded throughout a sample of 1 cm^2, so that pore size ranges from 1.5 to 2.8 μm.

The presence of diverse slightly polar groups at the end of the PS chain, its M_w = 84 KDa, and a polydispersity index of 1.7 probably account for the neat aptitude showed by this polymer to give ordered BFs in different casting conditions. What we experienced may appear partially in contrast with what recently was observed by Billon et al., who found that formation of highly structured films is promoted by ionization of the low molecular weight PS carboxylic end group, which stabilizes the water/CS_2 interface.[21] Qiao and co-workers, on the other hand, demonstrated on star polymers that increasing the number of hydrophilic groups over a certain degree brings a decrease of regularity through the honeycomb structure.[14] The behavior showed by our polymer seems to confirm that a small difference of polarity between the terminal groups and the rest of the polymer chains is sufficient to ensure a perfect hexagonal arranged pore formation.

As for PST-NH_2, ToF-SIMS analysis of PST-NH-bodipy porous films revealed that the internal walls of the cavities are enriched with the bodipy group with respect to the bulk of the film (data not shown).

We have recently observed that after the thermal treatment of BF structures obtained from an amphiphilic block copolymer formed by a polyfluorene polar rod

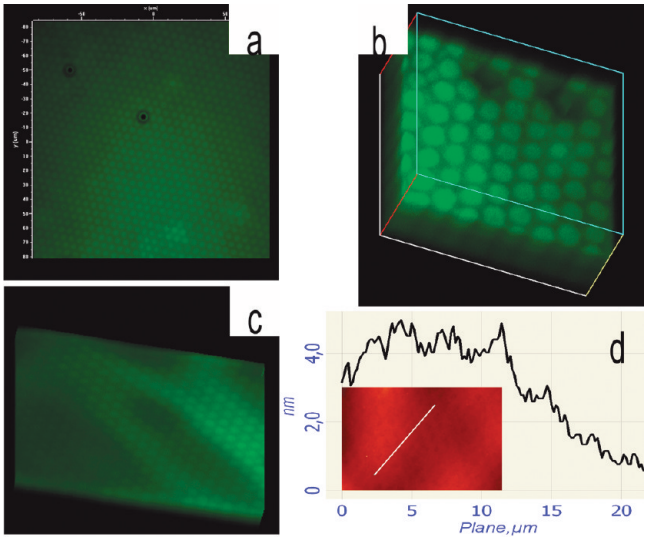

Figure 5. PST-NH-bodipy microporous film after heating to 135 °C for 2 h; (a) scanning confocal laser microscopy image; (b, c) 3-D reconstruction of *z*-scans done via confocal laser microscopy taken at two different magnifications; (d) roughness analysis measured by AFM along the white line (inset).

and a PS coil, an ordered array of fluorescent spots is formed on the film surface in the same position of the cavities left by water microdroplets.[33]

With the much simpler structure of PST-NH-bodipy, we have not only observed a similar phenomenon but also been able to optimize the procedure to produce ordered spotted surface films. In fact, because of the high degree of order obtainable in the hexagonal array of the pristine film, when the thermal annealing over the polymer glass transition temperature (T_g) causes the collapse of the BF structures and the material is brought from the internal surface of the spherical cavities to the outer surface of film, an array of fluorescent spots periodically arranged is obtained. AFM analysis confirmed that film roughness decreases (from micrometric porosity) to less than 3 nm, as shown in Figure 5-d.

In Figure 6 is shown a schematic representation of our explanation of this phenomenon. During the thermal treatment, the polymer starts moving from the bulk to fill the empty spaces. Consequently, film thickness decreases from about 3 to less than 1 μm, and the holes disappear. This implies that the fluorescent heads, which were preorganized around the cavity internal surface, compact themselves in a smaller surface (from spherical surface to disk) giving rise to a spot which is seen more fluorescent than the surrounding material.

ToF-SIMS analysis of the spotted flat film reveals a higher concentration of fragments related to bodipy residues coming from the fluorescent spots, thus indicating that really we are handling a functionalized surface (Figure 2-e). In some parts of the film, however, the signals from bodipy residues disappear, probably because in those regions the fluorescent spots are slightly dipped under the PS film surface during the closure of the pore.

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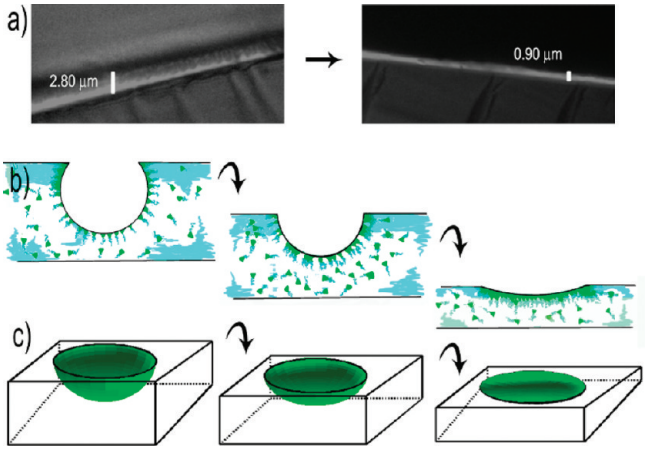

Figure 6. Transformation of a PST-NH-bodipy microporous film during thermal treatment (from left to the right). (a) Cross-section of the film placed on silicon substrate. (b) Sketched drawing of the cross-section of a pore. Green triangles stand for the bodipy fluorescent heads of the polymer. (c) 3-D representation of the same phenomenon.

Conclusions

We have shown that the BF approach is a suitable method to obtain films with cavities which can be functionalized. Two approaches have been reported and are based on the use of PS as a suitable material. In the first method, cavities with specific chemical functions are created. These can be easily obtained by using PS functionalized with polar groups. In this respect TEMPO modified with carboxylic, amino, and alcohol groups is a proper initiator to get functionalized PS suitable for the BF film formation. Because of the high concentration of specific chemical functions on the wall of the cavities, these are more prone than the film surface to react with other molecules. In this work we have shown that the cavities of a microporous film, obtained using an amino functionalized PS, can be evidenced using fluorescence microscopy after reaction with fluorescamine.

The second approach is based on the BF film formation starting with a PS already functionalized with a specific molecule. In this regard, we have used a bodipy-functionalized PS to get the BF film with cavities enriched by bodipy group. The thermal treatment of the film at a temperature over the PS T_g leads to a flat film with spots of fluorescent dye arranged in the same position where the cavities were in the pristine film.

Our group recently reported on zeolite-loaded BF holes in polymeric films.[34] Their formation is promoted when hydrophilic/hydrophobic properties of the crystals are enhanced through a chemical modification of the zeolites' external surface. In the light of the current study, a proper treatment of those hybrid BF films may give rise to interesting spotted hybrid surfaces.

We are currently expanding these approaches to biological molecules with the aim of obtaining ordered patterns suitable for biological tests.

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Supporting Information Available: Absorption and emission spectra, detailed AFM analysis after film thermal treatment, and GPC results for PST-NH-bodipy. This material is available free of charge via the Internet at http://pubs.acs.org.

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