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Interference lithography with functional block copolymer blends: Hierarchical structuration and anisotropic wetting

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ABSTRACT

This manuscript describes the preparation of hierarchically, i.e. micro and nanometer scale ordered surfaces with variable functionality by simultaneously combining the microfabrication using Laser Interference Lithography (LIL) and the self-assembly of block copolymers occurring at the nanometer scale. The block copolymers employed in this study are a double hydrophobic poly(2,3,4,5,6-pentafuorostyrene)-*block*-polystyrene ($P5FS_{31}$-*b*-PS_{21}) and an amphiphilic polystyrene-*block*-poly(acrylic acid) (PS_{20}-*b*-PAA_9) diblock copolymer. The incorporation of these block copolymers in the photosensitive mixture resulted in surfaces with hierarchically micro and nanostructured interfaces with either hydrophobic or hydrophilic surface chemical composition. Moreover, in comparison with microstructured surfaces prepared using statistical copolymer with similar composition, the use of block copolymers enhanced both the surface wettability changes and the final anisotropic wetting. We evidenced herein that by preparing unidirectional micrometer size patterns with either $P5FS_{31}$-*b*-PS_{21} or PS_{20}-*b*-PAA_9 the wetting anisotropy increases with the hydrophobicity or the hydrophilicity of the surface.

1. Introduction

Surface topography and functionality are two interfacial characteristics which largely determine the interaction of a particular material with its environment. On the one hand, previous studies demonstrated that the surface topography is a crucial factor for tuning the properties in nanostructured materials, such as adhesion/friction or the wettability of the surface. On the other hand, changes on the surface chemistry of patterned surfaces may provide surfaces with a broad range of additional potential applications in different fields such as catalysis, adhesion/lubrication, biorelated purposes or to produce biosensors just to mention few of them [1,2]. Therefore, in order to design a material for a particular application, both the surface morphology and the functionality should be considered. In this concern, several methodologies have been developed to fabricate surfaces with different topographical features with variable resolution and pattern dimensions. Lithography, laser ablation, chemical and physical etchings, self-assembly or mask stamping are among the most extended techniques [3–5]. Equally, the surface functionalization has been achieved by using, for instance, surface treatments including plasma or ozone treatments or by segregation of functional polymers [6,7]. However, examples

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involving the simultaneous surface functionalization and surface topography are rather scarce. Typically, these have been obtained by coating functional micro/nanoparticles onto planar surfaces. However, although the surface wetting have been modified, the use of such systems is limited due to reduced lifetime and stability of the particle coating that can be easily removed losing the surface functionality [8–10].

Herein, we present an interesting alternative to fabricate stable and functional and hierarchically ordered surfaces within one single step. For that purpose, lithography which is probably the most extended top down approach to generate micro and nanostructures on polymer surfaces will be employed. Lithographic approaches include many different alternatives such as photolithography, soft-lithography, e-beam lithography, interference lithography, embossing and printing lithography or scanning-probe lithography [11]. In order to fabricate surfaces with long range ordered patterns, interference Lithography (IL) has been recently employed to generate several large scale (cm^2) periodic designs and patterns with high resolution (down to the nanometer scale) with high accuracy and reproducibility [12–17].

In this manuscript, the formation of functional surface patterns made by IL and using functional block copolymers as additives in a photosensitive solution will be explored. In order to obtain functional interfaces, we employed a polymer blend composed of a commercial resin with either an amphiphilic block copolymer, i.e. polystyrene-*block*-poly(acrylic acid) (PS_{20}-*b*-PAA_9) or a double hydrophobic poly(2,3,4,5,6-pentafluorostyrene)-*block*-polystyrene ($P5FS_{31}$-*b*-PS_{21}) block copolymer. As will be depicted, after laser exposure and developing processes, a precise surface pattern in which the motifs have embedded the functional block copolymers has been obtained.

The addition of block copolymers offers two important advantages in comparison to random copolymers or even homopolymers. On the one hand, block copolymers tend to self-assemble upon appropriate annealing treatments thus allowing us to straightforwardly form nanostructured domains. On the other hand, the surface functionality provided by the reorientation of entire functional segments with either highly hydrophobic or highly hydrophilic domains exposed to the interface affects to a larger extent the surface wettability.

This study is focused on the preparation of micro/nanostructured line arrays, since in addition to the changes on the surface wettability these structures should exhibit anisotropic wetting behaviour. Anisotropic wetting involves the inhomogeneous distribution of a liquid and its accompanying wetting properties on a surface. Anisotropic wetting can have either a physical origin, when is attributed to liquid contact line encountering physical discontinuity (e.g., sharp solid edge) [18], or can be due to chemical heterogeneities present on the surfaces [14]. This interesting phenomenon has been studied for example in micro- and nanometer scale topographical surface structures (e.g., parallel lines, groves, wrinkles, pillars). Similarly, surfaces with chemical anisotropy (i.e. without any topographical pattern) such as parallel bands of chemical functionality with different surface energy may influence droplet wetting behaviour. Potential applications of such surfaces with anisotropic surface wetting include among others fluidic control and transport on microfluidic devices, directional self-cleaning coatings or antifouling surfaces and biomedical applications [19–22]. In addition, these materials have interest in evaporation-driven formation of patterns and are additionally interesting from a fundamental point of view [1].

Typically, as depicted below, the design of anisotropic surfaces has been carried out considering either the physical and chemical origin of the anisotropy. In order to combine both origins in the same systems, herein, we propose a strategy that combines both micro/nanostructuring and variation of the surface chemical composition.

2. Experimental

2.1. Materials

Styrene (S) (Aldrich, France, 99%), 2,3,4,5,6 Pentafluorostyrene (5FS) (Aldrich, France, 99%), and t-Butyl acrylate (tBA) (Sigma-Aldrich, Lyon, France; 98%) were distilled under reduced pressure over calcium hydride before use. Copper (I) Bromide (CuBr) (Sigma-Aldrich, Lyon, France; 98%), 2,2′-Bipyridyl (bipy) (Sigma-Aldrich, Lyon, France; 99%), N,N,N′,N″,N″,-Pentamethyldiethylenetriamine (PMDETA; Sigma Aldrich, Lyon, France; 99%), Phenylethyl bromide (PhEBr; Sigma-Aldrich, Lyon, France; 97%), and other solvents were used as received.

2.2. Synthesis of the block copolymers

The block copolymers employed in this study, i.e. Polystyrene-*block*-poly(acrylic acid) (PS_{20}-*b*-PAA_9) and Poly(2,3,4,5,6-pentafluorostyrene)-*block*-polystyrene ($P5FS_{31}$-*b*-PS_{21}) were prepared by ATRP as follows.

2.3. Synthesis of polystyrene-block-poly(acrylic acid) (PS_n-b-PAA_m)

The PS_{20}-*b*-PAA_9 (composition determined by ^1H NMR) diblock copolymers have been prepared in two steps following previously reported procedures [23].

2.3.1. Synthesis of polystyrene (PS_n-Br) macroinitiator by ATRP

All polymerizations were performed in Schlenk flasks previously flamed and dried under vacuum. ATRP was carried out using the following stoichiometry [S]:[I]:[CuBr]:[L] = 250:1:1:2, where S = Styrene, I = initiator (PhEBr) and L = ligand (bipy). The reactants were added under N_2 atmosphere. The reaction mixtures were then degassed by three freeze-pumpthaw cycles and placed