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Gradients of topographical structure in thin polymer films

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ABSTRACT

We report the fabrication of centimeter-long gradients of topography. Structured polymer thin films were made by spin-coating an immiscible poly(methyl methacrylate)/poly(2-vinylpyridine) (PMMA/P2VP) blend from a common solvent on a substrate presenting a surface-energy gradient. Due to the interplay between polymer-wetting of the substrate and polymer phase-separation, different morphologies were observed along the sample. Atomic force microscopy (AFM) revealed a gradual transition from a flat to a structured morphology as the surface energy of the substrate was reduced. The transition occurred for a well-defined range of surface energies. A selective solvent was used to remove one of the polymer phases, increasing the topographical contrast and providing insight into the different stages of the transition. Image analysis allowed a quantitative characterization of the structure gradient.

1. Introduction

The fabrication of gradients – usually chemical gradients, but also hardness, topography or size gradients – has been receiving increasing research interest in recent years. Gradients may form the basis of combinatorial studies, since a continuous range of properties is covered within a single sample. They may be used for practical purposes such as micro-fluidics, investigating biomolecular interactions, or studying nanotribology. Of particular interest is the application of gradients in cell biology. The use of gradients allows cell growth to be directly compared over a range of different surface topographies on a single sample and under identical conditions. This is particularly useful in biology, where achieving reproducibility is often challenging. Moreover, gradients can be used to study cell motility, an example being the recently studied locomotion of muscle cells on hardness gradients [1].

In this work, we focus on the fabrication of centimeter-long gradients of topography in thin polymer films. Some techniques for the creation of structure gradients in polymer films have previously been reported in the literature. The temperature dependence of polymer crystallization, polymer-film dewetting or phase separation of polymer blends has been studied using gradients of temperature [2,3]. Compositional gradients have also been fabricated using the interdiffusion of two polymer solutions [3,4]. By combining temperature gradients with composition gradients, two-dimensional gradients have also been produced [4,5].

In this study, we use the influence of surface energy on polymer-blend phase separation to induce gradients of topography. In films of polymer blends, the two interfaces (air–polymer and polymer–substrate) influence the demixing properties of the polymers [6–8]. There is an interplay between the phase separation of the polymers and the preferential interaction of one polymer with the interface, often leading to a wetting layer of one polymer on the substrate [9]. Differences in the structure of poly(styrene)/poly(2-vinylpyridine) (PS/P2VP) blends due to substrate surface energy were previously reported by Boltau et al. [10] using a substrate patterned into strongly hydrophilic and strongly hydrophobic areas.

As we aim at fabricating structure gradients, a substrate with a linear gradient in surface energy was used to screen a continuous range of surface energies. The substrate was prepared according to a previously published method and the structured thin film was fabricated using polymer demixing. Atomic force microscopy (AFM) was used to characterize the phase separation behavior of the polymer films as a function of surface energy. Image analysis allowed us to quantify the structural changes along the gradient.

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2. Materials and methods

2.1. Substrate preparation

Substrates with gradients of surface energy were fabricated as recently reported (Morgenthaler et al. [11]). Briefly, a gold-coated substrate was gradually immersed in a very dilute thiol solution to give a concentration gradient of adsorbed alkanethiols. A second alkanethiol was then adsorbed onto the free gold areas. The two alkanethiols were dodecanethiol [$CH_3(CH_2)_{11}SH$] and 11-mercapto-1-undecanol [$HO(CH_2)_{11}SH$], both purchased from Aldrich Chemicals (Milwaukee, WI). Ethanol (purity >99.8%, Merck, Darmstadt, Germany) was used as a solvent. The gold substrates were prepared by evaporating gold (purity >99.99%, Unaxis, Balzers, Liechtenstein) onto silicon wafers (POWATEC, Cham, Switzerland) at a pressure of about 2×10^{-5} mbar. All glassware was cleaned with piranha solution for 20 min and rinsed copiously with deionized water and ethanol. Attention: Piranha solution reacts violently with all organics and should be handled with care. The stock solutions were prepared by dissolving $CH_3(CH_2)_{11}SH$ or $HO(CH_2)_{11}SH$, in ethanol at a concentration of 0.005 mM.

2.2. Thin film preparation

A polymer blend of poly(methylmethacrylate) (PMMA) with poly(2-vinylpyridine) P2VP was dissolved in methyl ethyl ketone (MEK, Spectrophotometric grade, Sigma–Aldrich, Germany) at a concentration of 10 mg/mL, mixed at (50:50, w/w) PMMA/P2VP ratio and spin-coated (6000 rpm) onto the substrate. On evaporation of the solvent the solution phase separated to form a polymer film with a frozen-in, non-equilibrium microphase structure [12–15]. The polymers were purchased from Polymer Standards Service GmbH (Germany). Their properties are summarized in Table 1.

In some cases, a selective solvent was used to remove one of the polymers. Samples were dipped in ethanol (UVAsol ethanol from Sigma–Aldrich) for 1 min to remove P2VP and subsequently dried with nitrogen.

2.3. Characterization techniques

The gradients of surface energy were characterized by means of water contact angle measurements along the longitudinal axis of the gradient. Static contact angles were measured with a drop-shape analysis system (Krüss DSA 10).

Polymer films were characterized with AFM, using a Nanoscope Dimension 3100 (Digital Instruments/Veeco, Santa Barbara, CA). Tapping mode AFM was used for the characterization of topography using gold-coated silicon tips (typical force constant of 5.5 N/m) obtained from NT-MDT (Holland). Lateral force microscopy (LFM) was used for friction measurements with the same instrument but using SiN tips having a typical force constant of 0.06 N/m. Characterizations were performed in air at room temperature.

2.4. Image analysis

Different image analysis techniques were used to analyze the variety of topographies and transitions obtained. The topography was characterized in terms of roughness by means of R_q (also known as "RMS roughness"):

$$\mathrm{Rq} = \sqrt{\frac{\sum_n h_n^2}{N}}$$

where h_n is the height deviation from the mean data plane at pixel n and where N is the number of pixels in the image. The proprietary AFM software (Nanoscope III 5.12 r3) was used to measure the roughness on the images. Particle-size analysis was also performed on the images in order to calculate the mean area of the domains. The particle detection was carried out using AnalySIS software (Soft Imaging System GmbH).

Table 1
Characteristics of the polymers used

Polymer	Mw (Da)	Mw/Mn
PMMA	106 000	1.05
P2VP	79 100	1.05

3. Results and discussion

Gradients of structure in thin polymer films were fabricated using the influence of the surface energy of the substrate on the phase separation of polymer blends.

Flat silicon substrates with gradients of surface energy were first fabricated. Fig. 1 shows the water contact angles measured along the wettability-gradient substrate. A variation of the contact angle from 105° to 55° is observed over 1.5 cm. The polymer films were then spin-coated on these substrates.

After spin-coating the polymer blend films onto the substrates described above, the topographies of the films were characterized along the entire gradient, with measurements every 500 μm. In some cases, a selective solvent was used to remove the P2VP phase. Fig. 4 shows AFM images of the film, as cast, and after removal of the P2VP phase.

In the 'as cast' film (Fig. 4a), the topography of the film is clearly different at the hydrophilic and the hydrophobic ends of the sample. At the hydrophobic end, the polymer film consists of pits in a matrix, while at the hydrophilic end the film is very flat and laterally phase-separated domains are not observed. A gradual transition from one regime to the other takes place over a defined range of surface energies: from water contact angles of 95° to 75°. Outside this range of surface energies, no changes in the film topography are observed.

The transition in morphology observed from the hydrophobic to the hydrophilic end can be separated into three parts. At the hydrophobic extreme the polymer film consists of pits embedded in a matrix. Moving towards higher surface energies, the diameter of the pits increases and a change in their morphology is observed; from pits embedded in a matrix, the morphology gradually becomes bi-continuous. This constitutes the first part of the transition. In the second part, the bi-continuous morphology

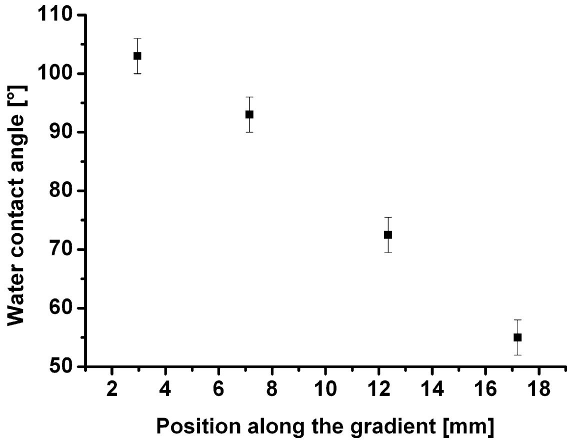

Fig. 1. Static water contact angle measurements along the gradient of surface energy.