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# Gradients of nanotopography in polymers

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# Summary

Materials with gradients in surface properties have been receiving increasing interest due to their importance in various applications. The fabrication of surface gradients is, for instance, an attractive approach to combinatorial studies, since a whole range of conditions can be examined on a single sample. This increases the throughput of the experiments and saves a great deal of time compared to conventional “one sample per condition” experiments. Surface gradients can also provide new properties to surfaces, for example the ability to move liquids or control biological cell locomotion.

This work is concerned with the development of gradients in topography in polymeric materials. A special emphasis has been placed on controlling the length of the gradients. The fabrication of structured surfaces employed the phase separation properties of polymer blends. More precisely, thin polymer blend films on surfaces were made by spin coating on a substrate, solutions containing a mixture of two polymers in a common solvent. During this process, the system phase-separates, leading to a thin structured polymer film on the substrate.

This technique, called polymer demixing, was chosen due to the numerous possibilities it offers for tuning the structure size and morphology.

Among the different parameters affecting the phase separation of polymer blend thin films, we focused on the influence of the surface energy of the substrate. The presence of the substrate/polymer interface can indeed modify the phase separation process due to the interplay between the wetting of the surface by the polymers and the phase separation within the film. A preliminary study was made using separate substrates of different surface energies in order to identify appropriate polymer blend systems. Depending on the polymer blends, different changes in topography were observed on varying the surface energy of the substrate. The next step was the fabrication of gradients of topography along the surface using surface energy dependence. This was divided in two main parts: the fabrication of gradients at the centimetre scale and the sub-millimetre scale.

The substrates with centimetre-scale gradients in surface energy were prepared following a procedure reported in the literature. Following the method, a gold coated substrate was gradually immersed in a dilute solution of methyl-terminated thiols, followed by backfilling with hydroxyl-terminated thiols. The polymer blend solutions were spin coated on these substrates and the resulting gradients in topography were characterized by means of atomic force microscopy. A gradual transition in topography was achieved for each polymer blend along the sample. The lengths and positions of the gradients in topography on the surface-energy gradients depended, however, on the polymer blend used.

For the fabrication of short gradients in topography, wettability gradients at the sub-millimetre scale had to be designed. The wettability gradients were realized using a novel combination of $TiO_2$ photocatalytic lithography with gray-scale lithography. A $TiO_2$-coated glass slide was brought into the vicinity of a surface functionalised with a thiol monolayer. On exposure to UV, the thiol monolayer was degraded due to the photocatalytic properties of $TiO_2$. By

designing a photomask with a short gray-scale gradient, the intensity of UV light illuminating the $TiO_2$ gradually varied along the sample, which resulted in a gradual degradation of the thiol monolayer. Polymer blend thin films were then spin-coated on these substrates to achieve short gradients in topography.

The last part of the study focused on the replication of gradients in topography in three different polymeric materials. Appropriate schemes for replication were developed in each case to ensure adequate structure transfer in each material.