Pattern Formation in Polymer Films by Non-Linear Processes

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SUMMARY: When a droplet of a dilute solution of a polymer is allowed to evaporate on a horizontal substrate, the polymer is deposited on the substrate as a regular 2 dimensional pattern of micrometer-sized polymer droplets or lines. It was found that the mechanism of the pattern formation involves a Bénard convection in the polymer solution and a regularly spaced fingering instability at the contact line of the solution with the substrate. By using liquid crystalline polymers, a novel hierarchic pattern can be observed.

Introduction

Pattern formation in polymer systems is attracting more attention within the past few years. From patterning on the molecular level, e.g. the micro phase separation of block copolymers, or the self-assembly of polymers at interfaces, to the top-down engineering by using photolithography, there have been many approaches in the polymer science field.

Even though nonlinear effects and processes (e.g. the Trommsdorff-Effect [1)], shear thinning, viscous fingering in the Hele-Shaw cell [2)], fingering due to the Marangoni Effect [3)], frontal polymerization [4)]) are well known in polymer science, they are rarely used for the preparation of polymer materials. Since nonlinear and dynamic processes may exhibit transient ordered structures, like Bénard convection cells in fluids or fingering instabilities at the edge of fluid droplets on substrates, they might be useful as self-organization processes for polymer films.

Here we show that it is possible to use the rich variety of dynamic processes that occur in an

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evaporating polymer solution to prepare ordered polymer patterns. The size of the obtained patterns is in the micrometer range, thus they are interesting for applications in the optics and electronics field.

Experimental Part

The pattern formation process and the pattern themselves were imaged by optical microscopy and atomic force microscopy. The experimental details are described elsewhere [5]. The poly-ion complex (**1**) was prepared as described before [12]. It contains 1 mol % of octadecyl rhodamine B as a fluorescent marker. In the case of the liquid crystalline polymer (**2**), an additional annealing process in vacuum was performed after the pattern had formed.

Results and Discussion

Typically 10-100 µl of the polymer solution (at concentrations of 0.1 – 1 g/l) were placed on a substrate and the resulting droplet had a diameter of several mm to a few cm. After the equilibration of the contact angle the edge of the droplet started to recede, due to the beginning of the solvent evaporation. Soon after the process starts, a fingering instability develops at the edge of the solution droplet (Fig. 1).

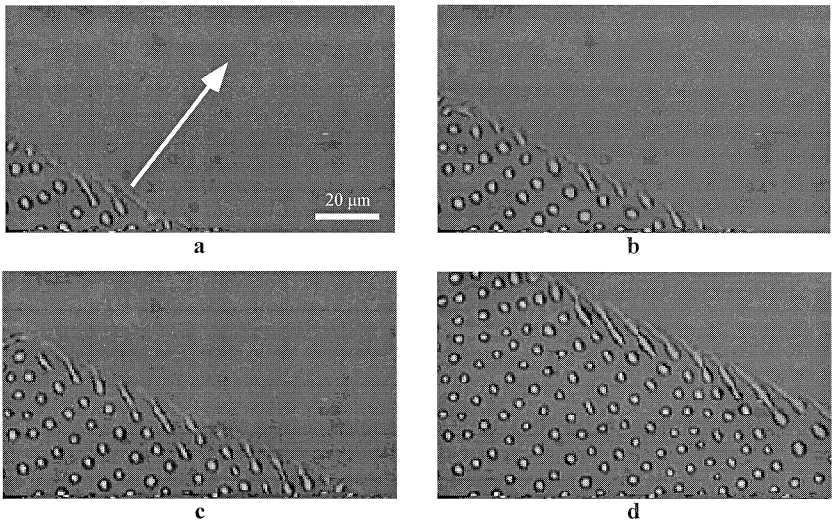


Fig. 1. Optical micrographs of the edge of an evaporating solution of polystyrene in benzene on silicon. The time between the video frame a) and d) is ca 800 msec. Scale bar: 20 µm

This instability is characterized by a regular modulation of the three-phase-line (also called contact line, where the solid substrate, the liquid polymer solution and the gas phase coincide) perpendicular to the macroscopic direction of the droplet edge. The reason for this ordered structure lies in the fact that the evaporation of the solvent is accompanied by a cooling of the solution surface, due to the heat of evaporation. The developing temperature gradient leads to the fingering instability [2]. When the solvent evaporates further, the fingers get more extended and a 'bottleneck' formation leads to the 'pinching-off' of small solution droplets (Fig. 1b). Finally, after all solvent has evaporated, the pure polymer is left on the substrate in the form of an array of droplets. When the wavelength of the fingering instability is in the same order as the pinching-off wavelength, a two dimensionally ordered polymer dot pattern is produced. The whole process basically does not depend on the nature of the polymer, nor on the solvent, and we could show that many different materials can be patterned in such a way [5-11]. We could prepare polymer patterns with dot diameters in the micrometer-size range. It was found that with increasing concentration the size of the aggregates gets larger, whereas the ratio between size and inter-aggregate spacing stays approximately the same. Higher casting temperatures lead to smaller patterns, which can be explained by the faster evaporation of the solvent, which leaves less time for the temporal coarsening of the fingering instability [5]. The smallest obtained patterns consist of polymer aggregates with a diameter of 100 nm, a height of 5 nm and an inter-aggregate spacing of 1 μm (Fig. 2). The left picture is the documentation of the high order of the deposited aggregates, whereas on the right side, a single polystyrene dot is imaged.

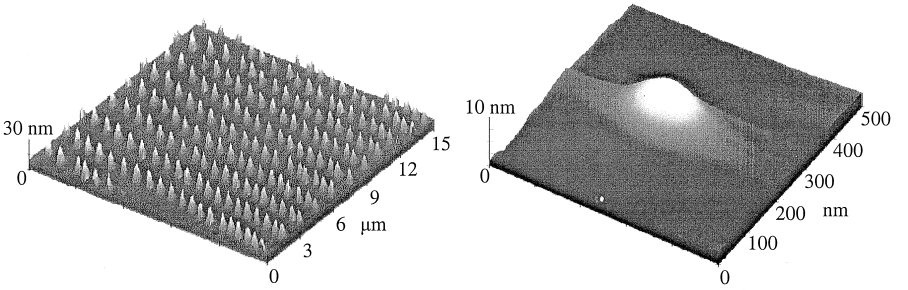
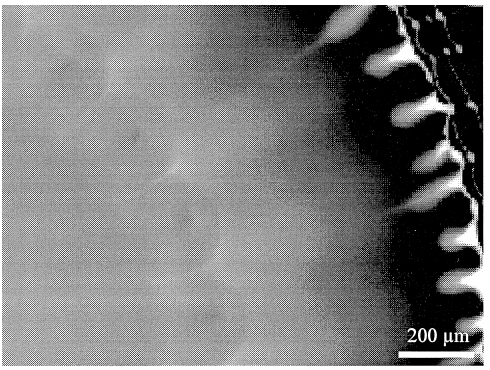


Fig. 2. Atomic Force images of polystyrene aggregates after casting a droplet of a 20 mg/l benzene solution of polystyrene (M_n 10000 g/mol; M_w/M_n = 1.05) onto mica.

Screening substrates, it was found that flat hydrophilic substrates (such as freshly cleaved mica and silicon covered by its natural oxide layer) give more regular structures than rough surfaces (such as quartz, glass slides, ITO, sputtered gold, etc.). The reason for this lies in the fact that a smooth receding of the three-phase-line has the least disturbance on the fingering

instability. On a rough substrate the fingering instability is disturbed due to the 'pinning' of the three-phase-line at surface heterogeneities and the resulting stick-slip motion leads to an irregular deposition of the polymer.

In order to get monitor the concentration distribution of the polymer inside the polymer solution, a fluorescence labeled polymer was used. Fluorescence microscopy revealed that the polymer distribution in the solution droplet is inhomogeneous (Fig. 3). In the center of the droplet, a string of circular structures with a diameter of 200 micrometer can be seen. These structures are highly mobile and sometimes they fuse or new rings are formed, similar to the well known Bénard convection cells. At the edge of the droplet, close to the three-phase-line, a series of bright stripes can be seen, which indicate a very high local polymer concentration. It is known that with increasing concentration of the polymer solute, the surface tension of the solution decreases, thus the solution tends to spread, i.e. develops a 'finger', at places with high concentration. It is also possible that the high polymer concentration-at the fingers lead to an increase of the viscosity and thus to a lagging of the finger behind the receding three-phase-line.



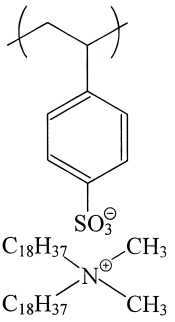


Fig. 3. Fluorescence micrograph (G excitation) of a droplet of a 1 g/l chloroform solution of the polyion complex **1** on glass. 1mol % octadecylrhodamine was added to the polymer as a fluorescence marker.

The aggregates formed from amorphous polymers show a smooth surface and a spherical shape (Fig. 2). In contrast, when a liquid crystalline polymer is used for patterning, each polymer aggregate shows an internal structure, that is different from the bulk liquid crystalline phase. A freshly cast sample of a liquid crystalline polyacetylene [13] was heated in vacuum above the clearing temperature of the polymer (165 °C) and subsequently cooled down to room temperature with a rate of 5 °C/minute. Aggregates that are larger than 500 nm

in height and 20 micrometer in diameter show a distinct surface topography in the central part, that is surrounded by an unstructured rim. The depth of the hexagonally ordered dents is a few nanometer. In situ optical microscopy revealed that at the dent structure is directly related to the onset of the liquid crystalline smectic A phase. Control experiments with nematic polymers showed no dent formation. Fast cooling leads to a conventional broken-fan-type texture, which upon annealing above the glass transition temperature converts to the dent structure, that is the thermodynamically stable phase.

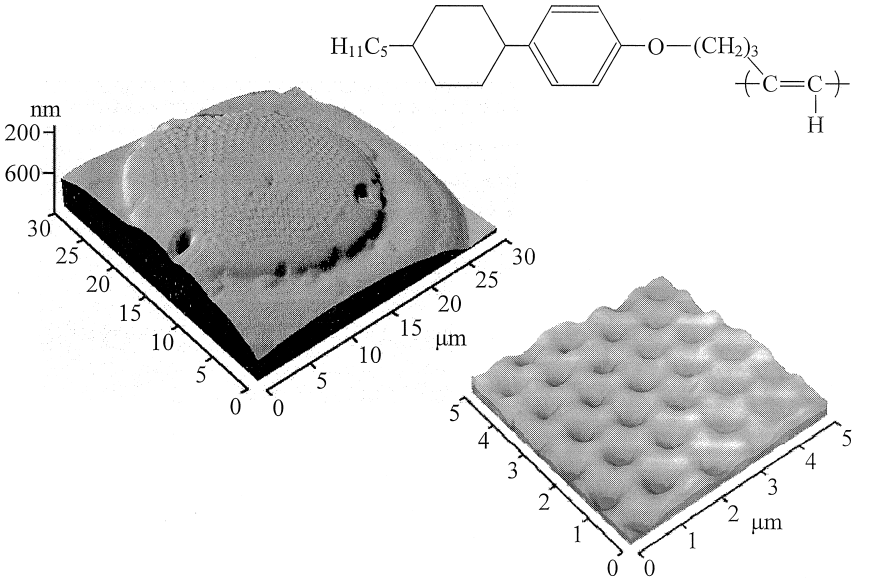


Fig. 4. Atomic force images of an aggregate of the liquid crystalline polymer at room temperature after slow cooling from the isotropic melt. The right part is a close-up view of the center part of the aggregate.

On the origin of this structure, that shows birefringence between crossed polarizers, can only be speculated: the structureless rim and a lower critical size of the height for dent-formation indicate that the structure is suppressed by the solid surface, even though the kind of surface (glass, mica, hydrophobized glass) has no effect on the dent-structure. On the contrary, the upper (free) surface of the aggregate is stabilizing the dent-structure, because the dent-structure does not appear when the sample is covered by a glass slip.

The use of phase-forming or phase separated polymers thus leads to the possibility of constructing patterns of polymers having a hierarchic structure, where each aggregate in a 2 dimensional patterns shows an internal ordered structure.

Conclusion

We could show that it is possible to form highly ordered arrays of polymer aggregates by a simple casting from dilute solution onto a solid substrate. The driving force for the self-organization of the polymer is a surface tension-driven instability at the edge of the solution droplet, as revealed by optical and fluorescence microscopy. The smallest obtained polymer aggregates have a diameter of 200 nm and a height of 5 nm. Using a liquid crystalline polymer, a novel surface modulation above a critical size of the aggregate could be found.

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