Polyelectrolytes on Block Copolymer Surfaces

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Summary: Soft lithography and properties of amphiphilic block copolymers are combined in a new technique for the generation of patterned substrates, which can be used in different ways as templates for further processing. In these processing steps the deposition of polyelectrolytes, metals and grafting from polymerizations are used for the construction of different structures.

Keywords: block copolymers; pattern; polyelectrolyte; soft lithography; structure

Introduction

In recent years a major interest in science focuses on size reduction and the build up of small and versatile structures in the nanometer range. A newer technique besides optical lithography emerged from the need for methods, which can be used in standard laboratories. Soft lithography[1] fulfills the requirements for such a technique because it is cheap and relatively easy to handle. We are combining the properties of block copolymers and soft lithography for the preparation of small structures.

The surface of block copolymers is made up by the phase with the lowest interfacial energy.[2] If the surrounding medium is changed this behavior can lead to a surface reconstruction.[3] The driving force for this reconstruction of the surface is the gain in surface energy due to the different interfacial energies of the polymer blocks. We want to use this effect in order to create hydrophilic hydrophobic patterns on films of amphiphilic block copolymers. For this purpose we combine the surface reconstruction of block copolymers with soft lithography (Figure 1).

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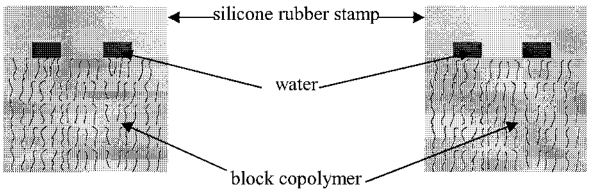


Figure 1. Scheme of surface patterning while (left) and after reorientation (right)

In order to obtain polymers with high mobility, poly(4-octylstyrene) with a Tg of –40 °C was chosen as hydrophobic block. The hydrophilic block will be prepared from 4-acetoxystyrene. The polymers were prepared by nitroxide controlled radical polymerization.[4] In the beginning a poly(4-octylstyrene) homopolymer is prepared. This can be used as a macroinitiator for the polymerization of 4-acetoxystyrene. The block copolymer can be deprotected by hydrazinolysis to give the amphiphilic poly(4-octylstyrene)-block-poly(4-hydroxystyrene) **(1,2)**. As a second system, which can be switched at elevated temperatures, poly(styrene)-block-poly(acetic acid 2-[2-(4-vinyl-phenyl)-ethoxy]-ethyl ester) **(3)** was prepared.

Table 1: Properties of amphiphilic block copolymers

Polymer	*Mw*	*PDI*	*ratio (hydrophilic/hydrophobic)*	*T_G hydrophobic phase*	*T_G hydrophilic phase*
				°C	*°C*
Poly(4-octylstyrene)-*block*-(4-hydroxystyrene)	53 000 63 000	1,44 1,48	10/1 **(1)** 1/1 **(2)**	-33	135
Poly(acetic acid 2-[2-(4-vinyl-phenoxy)-ethoxy]-ethyl ester)-block-(styrene)	63 000	1,36	1/2 **(3)**	101	-0,5
Poly(4-octylstyrene)-*block*-(2-[2-(4-vinyl-phenoxy)-ethoxy]-ethanol)	84 000	1,9	1/1,3 **(4)**	-24	14

The surface reconstruction of the polymer can be followed by changes of the contact angle. In the case of polymer **(1)** the molar ratio of the hydrophilic block is too high. The surface is already partly hydrophilic. The advancing contact angle drops only from 93° to 90° under water treatment. In the case of polymer **(2)** the surface is hydrophobic and the initial contact angle is 110°. During 24 h of water treatment, the contact angle drops down to 90°. The surface reconstruction is induced by the change of the surrounding medium. The water has a second crucial purpose in this process. Because of the high Tg of the hydrophilic polymer the reorientation should be hindered. The water acts as a softener due to the swelling of the hydrophilic block and so the Tg decreases below RT. If the water is removed and the sample is stored in air at room temperature, the contact angle does not switch back. This is due to the deswelling of the polymer, which causes an increase of Tg. The deswelling process is much faster than the reconstruction process and so the surface stays hydrophilic. If the sample is heated to 150 °C, which is above the glass transition temperature of poly(4-hydroxystyren), the value rises to 110° again.

A direct measurement of the change of the surface chemistry can be achieved by near edge x-ray absorption fine structure (NEXAFS) spectroscopy. In this x-ray experiment only the first few nanometers of the sample are probed. By excitation of the ^{1}s electrons into non binding orbitals, even the chemical surrounding of the excited atom can be determined. For the experiments polymer **(3)** were chosen because not only the oxygen content in the hydrophilic block is much higher. Also the carbonyl group has a strong and well distinguishable signal in NEXAFS measurements. The third reason for our choice is the difference of the concentration of the aromatic rings, which is quite large as well. The surface of freshly spin-coated polymer **(3)** is hydrophilic despite the fact that the hydrophobic block has the lower surface energy to air. To reach equilibrium the samples are tempered at 120 °C for 14 h and during this time the hydrophobic block appears at the surface. This can be seen in the high value for the aromatic C atoms. If the film is treated with water at 70 °C the surface reconstructs. An increase for the C-O and C=O bonds can be observed, whereas the signal for the aromatic C-atoms decreases. This can be explained by the exchange of the hydrophobic by the hydrophilic block. The same behavior can be found, if the total electron yield is measured (Figure 2).

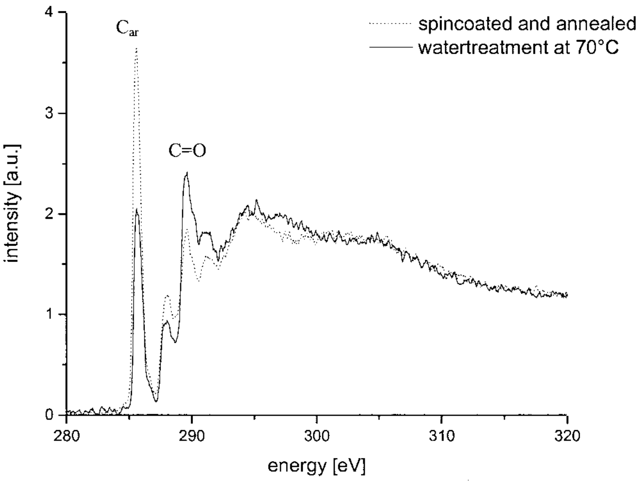


Figure 2. NEXAFS measurements of polymer **(3)** before and after reconstruction

If the sample is heated under nitrogen to 100 °C the values change back to the initial hydrophobic state.

The reorientation capability of amphiphilic block copolymers can be used to create hydrophilic hydrophobic structured interfaces. For the patterning process itself two different methods can be used. In the case of polymer **(4)** an exchange of the interface at room temperature can induce the reconstruction of the surface. This process can be started by using a structured hydrophilic poly (dimethylsiloxane) stamp (PDMS-stamp), which is brought into contact with the polymer surface. This stamp is created by pouring Sylgard 184 (Dow Corning) on top of a silicon master. After curing the mixture at 80 °C the stamp is hydrophilized in an oxygen plasma. Because of the low Tg of both polymer blocks the created surface pattern is not as stable as with polymer **(2)** mentioned above and will vanish in a much shorter time.

Polymer **(2)** can be structured with hydrophobic PDMS-stamps in the presence of water. The water creates the hydrophilic interface, which leads to the reconstruction in these areas. The PDMS covered parts remain hydrophobic and so a hydrophilic hydrophobic structured surface is obtained. The partially modified polymer film is still able to do the same reconstruction in further steps. In this way it is possible to obtain much more complicated structures. Another advantage of this method is that the structuring process works without any ink, which is in difference for a lot of other patterning techniques. Despite the advantage of the high stability of the pattern in contrast to the structuring process without water one major disadvantage exists. Because the water creates the hydrophilic interaction the structures on the stamp have to be connected so that water can flow into the created channels. This does not allow the fabrication of closed hydrophilic structures like spheres, squares or similar patterns.

Hydrophobic hydrophilic patterned surfaces, generated with this technique, feature OH groups in the hydrophilic parts. Beside the surface energies these OH groups can be used for a further chemical differentiations. This allows in addition to coulomb or van der Waals forces the build up of covalent bonds and the possibility to fix compounds permanently.

Because of the reconstruction process and swelling of the polymer the surface in the hydrophilic parts is not as smooth as it was initially. This height profile depends on the volume fraction of the used polymer blocks as it can be seen in (Figure 3). Polymers with higher content of the hydrophilic block show much larger height profiles. This can be understood because the swelling occurs in this block only and much more water can be absorbed.

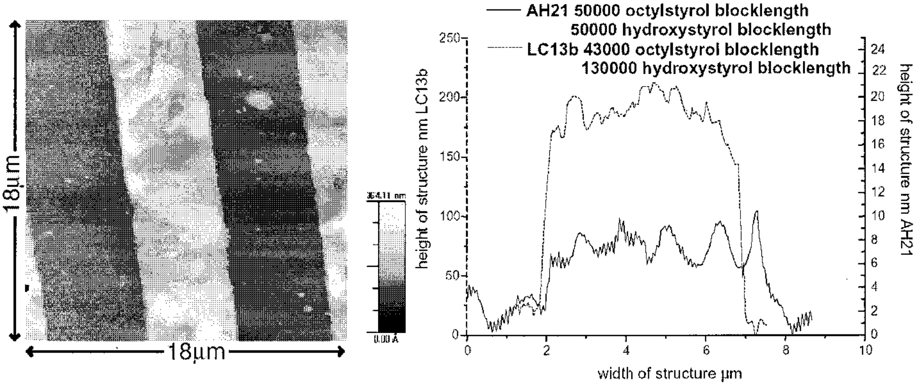


Figure 3. Height profile of 5µm structures in reliance on the polymer composition

To deposit polyelectrolytes on a patterned block copolymer surface charges have to be generated. Because of the ability to deprotonate the phenolic groups of the block copolymer the reorientation was done in an alkaline solution. The coulomb forces inside the film lead to an increase of the height difference between the modified and unmodified polymer parts. This can be seen if an alkaline solution is used for the patterning process instead of water (Figure 4).

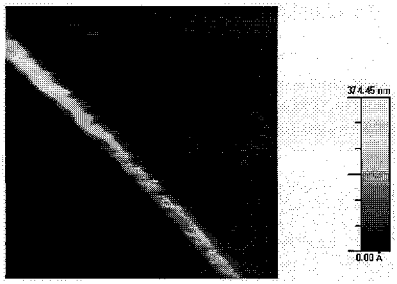
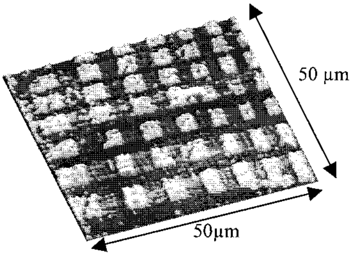
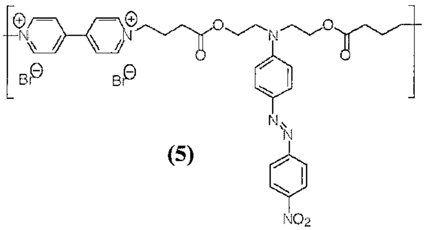


Figure 4. Height profile of a 5µm line prepared by reconstruction with alkaline solution **(2)**

To limit this effect it is possible to deprotonate the OH groups on the surface after reconstruction. For this purpose a structured substrate is dipped into a NaOH solution for a few seconds. To such a modified surface, which bears negative charges, polycations can easily be attached.[5] With this strategy it is possible to deposit cationic polyelectrolytes like polymer **(5)**[6] or **(6)** on a structured surface of polymer **(2)**. Another way to obtain various structures is to use a stamp to create a hydrophilic hydrophobic structured surface and then use a stamp as a mask for the following modification process. A similar pattern was created by Hammond et al.[7] They stamped the polyelectrolyte directly to the surface. Our microfluidic approach is more versatile because it does not depend on the interactions between the stamp and the polyelectrolyte. The deposition in squares of polyelectrolyte **(6)** is shown in Figure 5. A stamp with a line pattern was used to create a prestructured surface and after deprotonation with a 0.002M NaOH solution the stamp was put back onto the surface rotated at an angle of 90°. Now a 10^{-3} M solution of polyelectrolyte **(5)** in 1N HCl was brought in front of the lines and sucked into them by capillary forces. After 40 min the stamp was removed and washed three times with millipore water. It can be seen in (Figure 6) that the polyelectrolyte was deposited on the negatively charged parts.





(5)

Figure 5. Deposition in squares of polyelectrolyte **(5)** on top of a 5μm line pattern **(2)** with a 90° turned stamp

Due to the azobenzene sidegroups polycation **(5)** might be used as an alignment layer for liquid crystals. As azo-dyes orient by irradiation with polarized light, it should be possible to control the director of the liquid crystal by the direction of the polarized light. This is known as the "command surface effect".[8]. The polymer pattern was covered with a commercial liquid crystalline mixture (ZLI 4431®, Merck). Figure 5 shows a polarized light micrograph of a sample of polymer **(2)** covered with squares of polycation **(5)** (Figure 6). A grid of planar aligned areas, which shows birefringence, surrounds dark squares with homeotropic alignment. This observation can be explained by the molecular structure of the liquid crystals. The liquid crystalline mixture mainly contains molecules with cyano end groups. This leads to a negatively charged head. If the molecules come into contact with a positively charged surface, the heads are attracted. The result is a homeotropic arrangement of the mesogens. In the case of a negatively charged surface the molecules seem to orient side on, because the aromatic rings carry a slightly positive charge. The same planar alignment is achieved with a hydrophobic surface. Due to these interactions with different surface areas, liquid crystals can be used to visualize surface patterns.

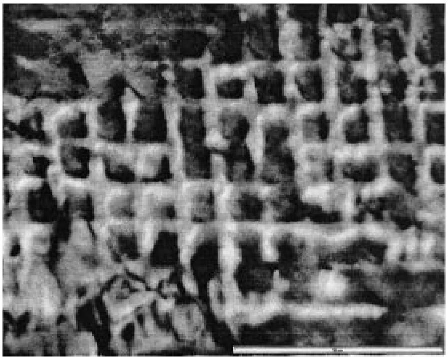
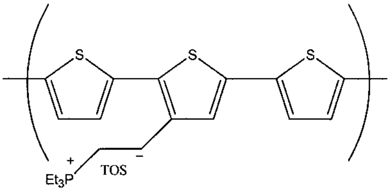


Figure 6. Pattern from Figure 5 covered with an LC mixture. Squares with homeotropic alignment and lines with planar alignment can be distinguished. (scale is 50µm)

The deposition of a thiophene polyelectrolyte onto a line shape structured polymer film of polymer **(2)** is shown in (Figure 7). The most interesting property of this kind of polymer is the conductivity of the thiophenes. For the deposition of polyelectrolyte **(6)** the substrate with structured polymer **(2)** is dipped in a 0.1g/ml aqueous solution of sodium hydroxide for 5 seconds. After this the deposition itself is carried out with a 10^{-2} mol/l solution of the polyelectrolyte in water with 10% ethanol.



(6)

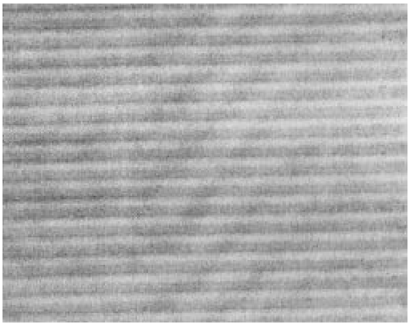


Figure 7. Deposition of thiophene polyelectrolyte on 5µm structured polymer **(2)**

As mentioned before the OH groups on the surface of the polymer film are also accessible for chemical reactions in general. In addition to the mentioned deposition of polyelectrolytes, esterifications followed by grafting from polymerizations[9] or deposition of metals are done so far (Figure 8). The deposition of copper[10] for example is a multistep process in which first of all Sn^{2+} ions are coordinated to the oxygen atoms of the surface and in a second step Pd is deposited by reduction to the defined regions. The Pd atoms work as a catalyst for the copper deposition from a Cu^{2+} solution with formaldehyde. The produced copper pattern is very stable on top of the polymer film and it is not possible to remove it from the polymer film.

Figure 8. Deposited copper left 5 μm lines of polymer **(2)** right: 10 μm triangles of polymer **(4)**

Conclusions

Amphiphilic block copolymers were prepared by nitroxide mediated polymerization of 4-octylstyrene and 4-acetoxystyrene. They can be patterned by bringing them in contact with a hydrophilic/hydrophobic interface. After deprotonation negatively charged surfaces are created. They can be decorated with polycations. Additional functionalities could be incorporated into the polymers. Polythiophenes allow the generation of patterns with conductive polymers. Liquid crystals could be used to visualize the surface pattern.

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