Ordered Self-Assembly of Nanosize Polystyrene Aggregates on Mica

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The formation of ordered patterns of nanosize polystyrene aggregates was observed by atomic force scopy. The samples were prepared by simply rinsing a mica surface with a dilute polymer solution in benzene.

Pattern formation is of great interest for both basic and applied research. For application in electronics, patterns in the sub-meter range have to be produced. In order to achieve this highly elaborated procedures using lithographic techniques had to be developed.

Recently, several reports have been published about the formation of patterns in thin polymer films on surfaces. In all cases blockcopolymers containing a hydrophilic and a hydrophobic block were casted onto hydrophilic surfaces.[1-4] The main driving force for the pattern formation is the demixing of the blocks in the copolymer.[5] In all these cases the polymer aggregates have dimensions in the sub-micrometer range. For homopolymers such a pattern formation was not reported yet.

Here we want to report a simple method for the production of ordered patterns of a polymer on a solid substrate. The preparation of the patterns is achieved by simple rinsing of a dilute polymer solution over a flat mica surface. No pre- or post-treatment of the mica surface is necessary. The obtained aggregates are in the sub-micrometer range and can form regular patterns.

Polystyrene (Mw 2630, 5970, and 9800 g/mol; Mw/Mn < 1.05 for all samples) was purchased from Aldrich, benzene was Uvasol Grade from Merck, Germany. All glassware was thoroughly cleaned with detergent solution (dcn 90, Decon Laboratories, England) followed by immersing in alkaline water/ethanol (1:1) with sonication. Mica was cleaved immediately before the rinsing process. AFM images were taken in the AC mode, in which a vibrating tip is scanned over the surface (Olympus NV 2500 aqac). This mode ensures that soft and only weakly bound materials are subject to only small forces from the probing tip.

For the sample preparation, freshly cleaved mica was rinsed with dilute benzene solutions of monodisperse polystryrenes. The mica was held at an angle of 60° during the rinsing process. The samples were allowed to dry in air for a few minutes and were directly subjected to analysis with the atomic force scope.

Regular patterns of polymer aggregates can be found for all samples using benzene solutions of monodisperse polystyrenes. Figure 1 shows a typical AFM image of polystyrene with a molecular weight of 9800 g/mol at a concentration of 20 mg/l in the rinsing solution. One can clearly see the formation of polymer aggregates which are well separated from each other. In this sample the aggregates are aligned on lines which are oriented perpendicular to the rinsing direction. The inter-line distance is constant, but the inter-aggregate distances within one line varies. The lines show a very large long range order of more than 10 μm. The 2 D Fourier transform power spectrum shows two sharp, slightly off-meridian maxima which are related to the long range ordering of the aggregates in lines. The distances of the aggregates within one line can be seen only as a diffuse halo.

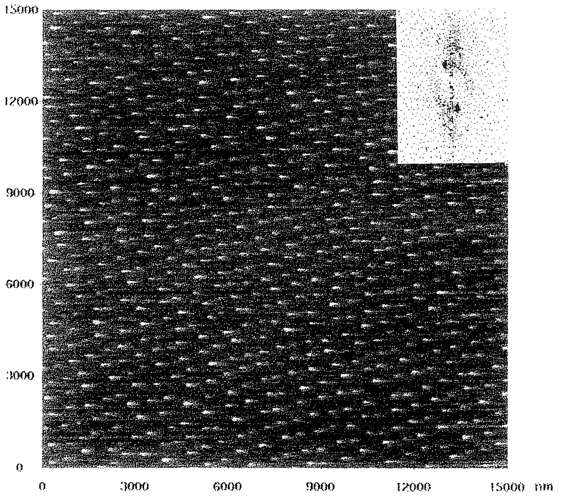

Figure 1. 15 x 15 μm^2 AFM scan of a mica surface rinsed with a polystyrene solution in benzene (20 mg/l). The grey scale is 2.4 nm. The inset shows the 2D Fourier spectrum.

The diameter of the aggregates is in the range of 300 nanometer with an average height of 1.7 nm. The histogram in Figure 2 shows that the height distribution is narrow and centered round 1.7 nm with a full width at half height of only 0.3 nm. Generally, the size and height of the aggregates and also the inter-aggregate distance depend on the molecular weight of the polymer and the concentration in the rinsing solution. Higher molecular weight and higher concentration lead to larger aggregates. With higher concentration the inter-aggregate distance decreases.

Figure 3 shows a closer view of the same sample at a different location. One can clearly see a hexagonal ordering of the polymer aggregates. The aggregates have a diameter of 296 ± 54 nm, a height of 6.7 ± 0.8 nm and the inter-aggregate spacing is approximately 1 μm. Although the coherence length of the

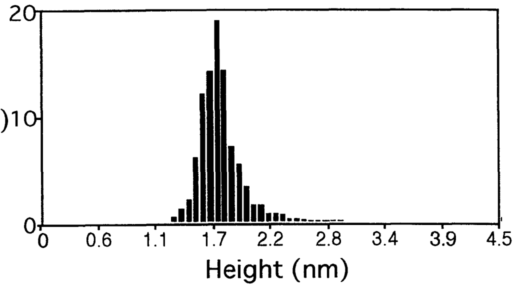

Figure 2. Histogram of the height distribution of the aggregates of Figure 1.

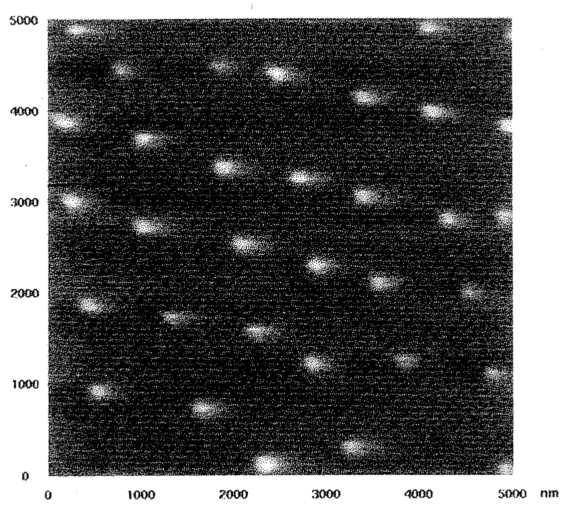

Figure 3. 5 x 5 μm^2 AFM scan of a mica surface rinsed with a polystyrene solution in benzene (20 mg/l). The grey scale is 9.5 nm.

hexagonal pattern is in the range of only a few μm, similar patterns can be seen at several places of the sample, thus this is not a singular structure.

Rinsing the mica with higher concentrated benzene solutions of polystyrene, an ordered structure of separated polymer aggregates cannot be formed. In some of these samples, separated aggregates coexist with a partial network structure in which aggregates are interconnected, leading to H- and Y-shaped structures. At concentrations as high as 100 mg/l of polystyrene with a molecular weight of 9800 g/mol, a ruptured film which contains holes is formed.

The driving force for the observed aggregate formation is the dewetting of the hydrophobic polystyrene from the hydrophilic mica.[6] Different stages of the dewetting of high molecular weight polystyrene from hydrophilic silicon oxide surfaces were observed by annealing a spin coated polystyrene film for different times at elevated temperatures.[7] The dewetting starts with a hole formation in a flat polymer film. Further heating and dewetting leads to the formation of a polymer network, which collapses at even longer annealing times. The thus formed polymer aggregates on the surface show no ordering.

Even though we can only investigate the final stage of the dewetting for our samples under the AFM we would like to propose a similar mechanism for dewetting as in Ref. 7.:

During the evaporation of the thin benzene film which remains on the mica surface after rinsing, a thin polystyrene film is produced. This film may still contain solvent and is highly mobile. Instantaneous rupture due to the very high surface energy of this film leads to a network structure. This structure equilibrates in that way that the surface energy of the polystyrene is minimized. Finally a regular network of strings containing polystyrene is formed. Rupture of this network at its weakest points leads to the formation of the separated polymer aggregates.

The ability of pattern formation depends of course on the type of polymer, the surface and also on the used solvent. In another set of experiments we could show that dendrimers of the benzyl alcohol-type[8,9] can also form these patterns.

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