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Kondensierte Materie

Großgeräte der physikalischen Grundlagenforschung

Schlussbericht vom 28.06.2004 zum Thema:

Charakterisierung und Optimierung von Nano-Templaten aus Polymeren

Zuwendungsempfänger:	Institut für Polymerforschung Dresden e.V. (IPF)
Projektleitung:	Prof. Dr. M. Stamm
Förderkennzeichen:	05KS1BPA/4
Förderzeitraum:	01.04.2001 – 30.09.2004
Zuwendung:	184.771,00 EUR
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Genutzte Großgeräte:

BESSY - BESSY

DESY - DORIS

Angaben zum Projekt:

Veröffentlichungen:	4
Konferenzbeiträge:	11
Diplomarbeiten:	0
Dissertationen:	1
Habilitationen:	0
Patente:	1

Das diesem Bericht zugrundeliegende Vorhaben wurde mit Mitteln des Bundesministeriums für Bildung und Forschung gefördert. Die Verantwortung für den Inhalt dieser Veröffentlichung liegt beim Autor.

Schlussbericht-Kurzfassung

Zuwendungsempfänger: ***Institut für Polymerforschung Dresden e.V. (IPF)***

Projektleitung: ***Prof. Dr. Manfred Stamm***

Charakterisierung und Optimierung von Nano-Templaten aus Polymeren

We synthesized block copolymer supramolecular assemblies (BCA) based on the selective hydrogen bonding of the low molar mass additive (2-(4'-hydroxybenzeneazo)benzoic acid, HABA) with the vinylpyridine block of poly(styrene-*block*-4-vinylpyridine) (PS-PVP). First, we investigated bulk properties of the BCAs. We characterized microphase separation of the BCAs with small angle X-ray scattering (SAXS) and hydrogen bonding of HABA with PVP block by FTIR and UV-vis spectroscopy and wide angle X-ray scattering. It was shown that methanol is selective solvent for HABA. Extraction of HABA with methanol allows to remove the additive from the BCA and to obtain nanotemplates. The nanotemplates provide significant electron density contrast (polymer vs. air) as compared with BCAs. We found that the periodicity of the nanotemplates is on the range of 25 to 32 nm depending on the block copolymer molecular weight and characteristic morphology (cylindrical or lamellar). The results of the investigations “in bulk” are in good agreement with the findings of O. Ikkala. Thus, we focused our efforts on the investigations of thin films of BCAs as a novel approach to nanotemplating and nanopatterning.

We found an unexpected behavior of the supramolecular assemblies of PS-PVP block-copolymer with HABA molecules resulting in the perpendicular alignment of cylindrical or lamellar nanodomains. The alignment is insensitive to the composition of the confined surface. The films can be reversibly switched from the perpendicular to parallel orientation and vice versa upon exposure to 1,4-dioxane and chloroform vapor, respectively. The re-alignment in different solvents is a relatively fast (tens of minutes) process. The perpendicular orientation of the cylinders/lamellas can be approached without applying of strong external stimuli (e.g. electrical field) which is in a contradiction to the surface reconstruction effect usually observed for thin films of block copolymers. The combination of AFM, XPS, XPEEM, GISAXS, ellipsometry and X-ray reflectometry allowed us to investigate the fine structure of thin films of the BCAs and to explain the apparent contradiction. We suggested two motifs. The first one is dynamics of swelling which forces the system to change morphology depending on the swelling ratio and selectivity of the solvent in respect to major- and minor-phase forming blocks. The second one is the interfacial thermodynamics of the system. Specific intermolecular aggregation of HABA molecules can overcome the confining surface dominated reconstruction and stabilize the perpendicular alignment in 1,4-dioxane due to the self-adaptive behavior of SMA surface.

The walls of the nanochannels are formed by the reactive PVP brush. It allows to use the nanotemplate for physico-chemical and/or chemical controlled loading with different materials. We demonstrate that the channels can be filled with metals, electroconductive polymers, and organic species to obtain periodical arrays of nanodots/nanowires with valuable properties for various fields of nanotechnology.

Schlussbericht

Zuwendungsempfänger: ***Institut für Polymerforschung Dresden e.V. (IPF)***

Projektleitung: ***Prof. Dr. Manfred Stamm***

Charakterisierung und Optimierung von Nano-Templaten aus Polymeren

Participants:

Projektleiter: Prof. Dr. M. Stamm

Mitarbeiter: Dr. A. Sydorenko, Dr. S. Minko, Dr. I. Tokarev, Mr. R. Křenek

Target setting

The technical and scientific aims of the project comprised the following:

1. preparation of the polymer templates in the bulk with organized arrays of pores of cylindrical shape with pore diameter smaller than 20 nm and study the structure of the materials with SAXS, WAXS, GID, scanning X-ray microscopy and SPM.
2. Optimization of the structure with respect to molecular parameters (cylinder size, periodicity) and phase separation of self-organized supramolecular polymeric materials to approach the well organized cylindrical morphologies with controlled characteristic dimensions to ordered samples on a microscopic scale
3. Development and optimization of oscillatory shear flow method for the orientation of the supramolecular self-organized polymeric structures on a macroscopic scale in the bulk.
4. Removal of one component for the preparation of macroscopically ordered polymer templates at a nanoscopic scale.
5. Fabrication of thin films of ordered polymer templates by a similar procedure in thin copolymer layers
6. Characterization of structure and organization at different scales at each step of preparation by a combination of different techniques (if possible *in-situ*) and optimization of preparation conditions.

Conditions and schedule of the project.

The investigations in the frame of the project were performed on the experimental facilities of Insitut für Polymerforschung Dresden. The Institute is equipped with modern hi-tech instrumentation which allows to perfom world-class experiments, such as AFM microscopy and X-ray scattering/reflectivity. Also, some experiments were performed at large instrumentation at HASYLAB (GISAXS) and BESSYII (μ-NEXAFS, XPEEM). The work under the project was scheduled for three years in the frame of the BMBF Priority Programm "E*rforschung der kondensierten Materie"*.

Collaboration in the frame of the project.

In the frame of the project we collaborated with the research groups in Germany and established international scientific contacts. μ-NEXAFS and XPEEM study was performed in cooperation with Prof. D. Schmeisser, Brandenburgische Technische Universität Cottbus. GISAXS measurements and data analysis were performed together with Dr. Peter Müller-Buschbaum, Technische Universität München. Optical properties of additives and polymer assemblies were evaluated and discussed with the help of Dr. V. Cimrová, Institute of Macromolecular Chemistry, Prague, Czech Republic.

Scientific results

According to the plan described in the proposal, we performed the necessary investigations and obtained the scientific results as followed.

(I) Selection of the materials and investigation of formation and microphase separation of block copolymer supramolecular assemblies

On the first stage of the investigation we performed thorough search of the materials (block copolymers and additives) which satisfy to the following criteria: selective hydrogen bonding between one of the blocks of BC and additive, strong microphase separation, easy extraction of the additive, ability to form thin films, easy to visualize. We selected well-known block copolymer recently used by O. Ikkala for synthesis and investigations of supramolecular comb copolymer-like systems, i.e. poly(styrene-block-4-vinylpyridine). We used two samples of PS-PVP of different molecular weight: M_n^{PS} = 35500 g/mol, M_n^{PVP} = 3680 g/mol, denoted further as BC1, and M_n^{PS} = 32900 g/mol, M_n^{PVP} = 8080 g/mol, denoted further as BC2. As the additive we have chosen 2-(4'-hydroxybenzeneazo)benzoic acid (HABA) which possesses two polar groups capable to form hydrogen bonds with PVP block and azobenzene group with high molar extinction (azo-dye). The samples of equimolar HABA (in respect to PVP content) of BC1+HABA and BC2+HABA were investigated with FTIR, UV-vis spectroscopy and SAXS before and after HABA extraction. FTIR spectra showed formation of strong hadrogen bonds between HABA and nitrogen of PVP block. UV-vis spectroscopy gave strong evidence for H-aggregation of HABA (parallel face-to-face, according to the molecular exciton model). Moreover, UV-vis measurements showed complete extraction of HABA with methanol in 2 min. SAXS of BC1+HABA and BC2+HABA demonstrated typical scattering patterns characteristic for BC with the periodicity of 25.5 nm and 31 nm respectively. However, extraction of HABA results in drastic increase of the electron density contrast and, thus, sufficient increase of scattering signal. Noteworthy, the periodicity of washed samples was identical to the samples “as prepared”. The results obtained for BC1+HABA and BC2+HABA were similar to those found for PS-PVP with n-pentadecylphenol as reported by O. Ikkala. Therefore, we focused our next steps on the investigations of morphology and orientation of BCAs in thin films. The general concept of the BCA approach is shown in the Figure 1.

(II) Thin films of cylinder forming assembly (BC1)

BCA films on Si-wafers were prepared by either spin- or dip-coating. In optical microscope the polymer films with the thickness ranging from 20 to 100 nm (ellipsometry) are macroscopically and microscopically smooth and show no signs of HABA phase separation, such as crystals or stains. It suggests that HABA molecules are associated with PVP blocks building comb-like polymer chains. The AFM scratch test gives the same film thickness as ellipsometry if the BCA film is modeled as a layer with apparent refractive index n = 1.63. Such an elevated value of apparent refractive index as compared to that for PS-PVP (1.59) is attributed to significant fraction of HABA.

The detail investigation of BCA films with AFM shows the dependence of the morphology on the deposition conditions. BCA films deposited from chloroform solution demonstrate the terrace formation. The films are very smooth inside of the terraces with rms roughness of about 0.3 nm for 1×1 μm^2 lateral scale. In contrast, BCA films deposited from 1,4-dioxane are flat and featureless. The rms roughness is 0.15 nm as measured on 1×1 μm^2 lateral scale. We did not visualize the fine structure of the materials because of poor contrast between mechanical behavior of PS and PVP+HABA domains in the film.

As expected, methanol destroys supramolecular assemblies and removes selectively HABA from BCA leaving cylindrical cavities in the film. The AFM scratch test showed no

difference in film thickness before and after washing. It gives evidence that almost all HABA is located in PVP domains because the thickness of the PS matrix remains unchanged. Ellipsometric data for the same film thickness were fitted with the apparent refractive index n = 1.50 ± 0.01. Such decrease of n from 1.63 for BCA film (before washing) to 1.5 (after washing) is effected by the formation of porous morphology of the film due to the elimination of HABA. Note, that the obtained n value is much lower then n = 1.59 for the PS-PVP reference film which gives additional evidence for the formation of membrane with porous morphology. The estimated volume fraction of the pores in the membrane ($n_{PS} = n_{PVP} = 1.59$) is in good agreement with the concentration of HABA in the initial mixture (17.8 %). The rinsing with methanol develops the fine structure of the films clearly observed with AFM. The film deposited from chloroform shows well aligned stripes which can be assigned as C || cylindrical domains.

The film deposited from 1,4-dioxane and washed with methanol demonstrates caves of about 9 nm in diameter which are projection of C ⊥ domains (channels) with periodicity of about 25.5 ± 1.0 nm (Figure 2a). The center-center distance analysis reveals a relatively narrow distribution of spacing between channels with the standard deviation < 20 % as visualized by the Gaussian fit (Figure 2b) and Fourier-transform image (inset). The center-center distance distribution found for the membranes prepared from the “as deposited” films is comparable with the distribution of an optimized PS-PVP film obtained by the “neutral surface” approach. We observed the same level of order for different film thickness ranging from 20 to 100 nm. X-ray reflectivity gives strong evidence for formation of C ⊥ and C || patterns after swelling in 1,4-dioxane and chloroform, respectively. XPEEM shows completeness of the terraces in the case of C || and presence of PS block at the polymer-air interface. It is noteworthy, that the same behavior was found for substrates of *different chemical compositions,* for example PS brush, gold, ITO-glass, Ni. Thus, the film morphology is insensitive to the substrate surface nature.

Alignment of cylindrical domains in BCA films can be easily changed with appropriate solvent, for example, upon annealing of the 60 nm thick film deposited from 1,4-dioxane (C ⊥ pattern) in saturated vapor of chloroform for 30 min at room temperature. Once the sample was removed from the chamber, it dried in about 1 sec. Then we rinsed it with methanol. The film reveals the characteristic C || morphology similar to the morphology obtained directly after deposition from chloroform solution. Oppositely, BCA films deposited from chloroform with C || alignment were re-oriented into hexagonal C ⊥ morphology by annealing in 1,4-dioxane saturated vapor atmosphere for 30 min at room temperature (Figure 2). Moreover, swelling of the BCA film in 1,4-dioxane vapor results in a significant increase of order. The center-center distance distribution is very narrow (standard deviation 9 %). Six sharp first order peaks and the presence of higher order reflections are clearly seen on the FFT image demonstrating the almost perfect hexagonal order spreading over area of 0.2 - 2 μm^2. GISAXS out-of-plane scattering gives direct evidence for the re-alignment. We assume that the well ordered structure is promoted by aggregation of HABA molecules. The re-alignment occurring in BCA is reversible, relatively fast, and can be repeated several times for not rinsed films. Kinetics of the re-alignment was monitored by analyzing morphology of the films as a function of time and swelling degree (evaluated with ellipsometry). We found out that the re-alignment began upon exposure to saturated vapor of solvent if the swelling approached 2.5 times increase of film thickness (in our experiments this swelling degree was observed in 10 min). Then the completed re-alignment was approached in about 10 min. Very similar kinetics was observed for different solvents.

The experiments were performed in different solvents and we found out that the stability of the C ⊥ alignment increased with the increased reactivity of the solvent in formation of hydrogen bonds. For example, the C || alignment was found in toluene and chloroform. The SMA film deposited from THF exhibit a co-existence of C || and C ⊥ structures, while in 1,4-

dioxane the C ⊥ structure is stable. Solvent evaporation drives the BCA structure to adopt the perpendicular orientation. 1,4-dioxane is a solvent selective for the PS matrix. Swelling in 1,4-dioxane leads the system from cylindrical to spherical morphology. Solvent evaporation results in a shrinkage of the matrix in the vertical direction and subsequently merges the spheres into the vertical cylinders.

On the other hand, taking into account the above mentioned behavior and the structure of the SMA film we may speculate that the reversible and dynamic supramolecular aggregation between PVP and HABA via hydrogen bonds may introduce the mechanism of self-adapting of the interface composition. Redistribution of HABA molecules between bulk and interface occurs to approach a minimum interface energy for the particular alignment and environment, making the morphology to be insensitive to the confining surface. Solvent plays a very important role competing with PVP for HABA molecules so that a subtle interplay between HABA-PVP-solvent interface interactions may result in conditions to switch in the mechanism as it proved by the FFT spectra (Figure 2b). This mechanism helps to overcome surface dominant alignment as compared to BC films. The detail investigation of the mechanism requires consideration of many parameters and it is out of the focus of this paper. The prevalent role of HABA is the subject of our future investigations.

(III) Thin films of lamella forming assembly (BC2)

Similarly to BC1 based assembly, BC2+HABA assembly was synthesized. Thin films of the BCA demonstrate the lamellar structure as revealed by ellipsometry, AFM and X-ray reflectivity. As well, lamellar BCA shows strong tendency to realignment (switching) upon vapor annealing depending on the solvent used. Chloroform vapors induce parallel alignment with the typical for parallel alignment terrace formation (Figure 3). The height of the terraces amounts to 31 nm. Extraction of HABA results in sufficient decrease of the terrace height down to 21 nm, which correspond to the amount of HABA in the assembly (30 % by volume). In contrast, swelling in 1,4-dioxane results in the fingerprint-like pattern with the periodicity of 31 nm. After HABA extraction the groves are clearly seen. Ellipsometry of the washed films of the BCA reveals sufficiently lower refractive index of about 1.42; the index corresponds to about 30 % pore fraction according to the Bruggeman's equation. Both ellipsometry and AFM give evidence of switchable lamellar morphology of the BC2+HABA assembly.

(IV) Loading of nanotemplates

It is noteworthy, that the walls of the channels formed after rinsing with methanol are constituted from the brush of PVP chains. The free space left by HABA molecules can be reversibly occupied by swollen PVP chains upon exposure the membrane to selective solvent or acidic aqueous solution. Thus, the fabricated membranes belong to the class of smart membranes with uniform reactive channels of a narrow distribution in size.

The nanomembrane prepared by rinsing in methanol of the SMA film in the C ⊥ orientation on the gold coated Si-substrate was filled with Ni clusters. Nickel was introduced into the cylindrical channels of the membrane via electrodeposition method. Then we washed out the polymer template with THF. The well ordered lattice of Ni dots of 15-20 nm in the diameter, 10 nm in the height with 25 nm in the period was observed with AFM (Figure 4a). Taking into account the widening effect of AFM tip, the apparent size of the dots is in good agreement with the nanotemplate channel diameter (8 nm). Few defects (lacunas) appear in the array of Ni dots due to the non uniform electrodeposition kinetics of the metal clusters in nanochannels. Besides the potential application, this experiment gives evidence that the cylindrical channels cross the membrane from the top to the bottom.

Also, we performed electrochemical deposition of Ni through the BCA nanotemplate on Si{111} electrode. The deposition potential varies during deposition on the range of –1.0 V to

–1.05V at 0.3 mA/cm^2 current density applied in DC galvanostatic regime. We explain the overpotential increase as compared with Ni electrode by presence of thin film of SiO_2 native layer interfering the electrodeposition in DC regime. We believe this is the reason why electrodeposition in DC regime results in very rough covering consisted of Ni clusters of micron size. In deed, nucleation rate is much lower then growth and overpotential value is higher in case of insulating thin layer on top of the electrode. It results in fast growth of rare clusters and overload of the separated nanotemplate channels. To overcome the effect of insulating SiO_2 layer, we applied impulse galvanostatic regime as proposed by Gösele et. al. We modified the AC galvanostatic deposition parameters for thin nanotemplates and optimized the condition. Ni nanodots of 5 - 20 nm high are clearly seen as well as sufficient surface lacunas. The estimation of lacuna surface with flooding procedure gives the lacuna fraction on the range of 40 - 60 %.

The comparison of Ni electrodeposition conditions and morphology of nanostructures obtained on Ni and Si{111} demonstrates the effect of thin insulating layer on the deposition process. In order to visualize the found effect, we performed Ni electrodeposition onto mosaic Cr electrode partially covered with insulating layer of poly(1,2-butadiene) (PBD). For that, thin film of PBD with addition of 5 % of photoinitiator, i.e. benzophenon, was spin-coated onto Cr covered wafer and illuminated with UV light (365 nm mercury lamp) through TEM grid of 12 μm periodic square pattern. After washing with toluene, the 60 nm thick cross-linked PBD squares were revealed with large scale AFM. Micromapping ellipsometry showed that the shadowed location is free Cr surface. We deposited the SMA thin (70 nm) film on top of Cr mosaic electrode and completed it into nanotemplate with methanol rinse. Afterward, we performed Ni electrodeposition through the nanotemplate in galvanostatic DC regime (0.3 mA/cm^2, 1000 s) as described above and removed the polymer template in nonselective solvent (chloroform). Obtained samples were investigated with AFM and XPEEM.

The NEXAFS measurements of Ni deposition were performed prior the XPEEM measurements to find the exact Ni2p bonding energy as well as the peak width. The result of subtraction of XPEEM images before (851.5 eV) and after (854.0 eV) Ni2p peak from the image required at the Ni2p peak (853.0 eV) is shown on the Figure 4b. It undoubtedly demonstrates distribution of Ni in the space between the PBD masked electrode surface. Thus, we obtained two scale hierarchy patterning combining electrode photolithography with insulating layer and nanotemplating.

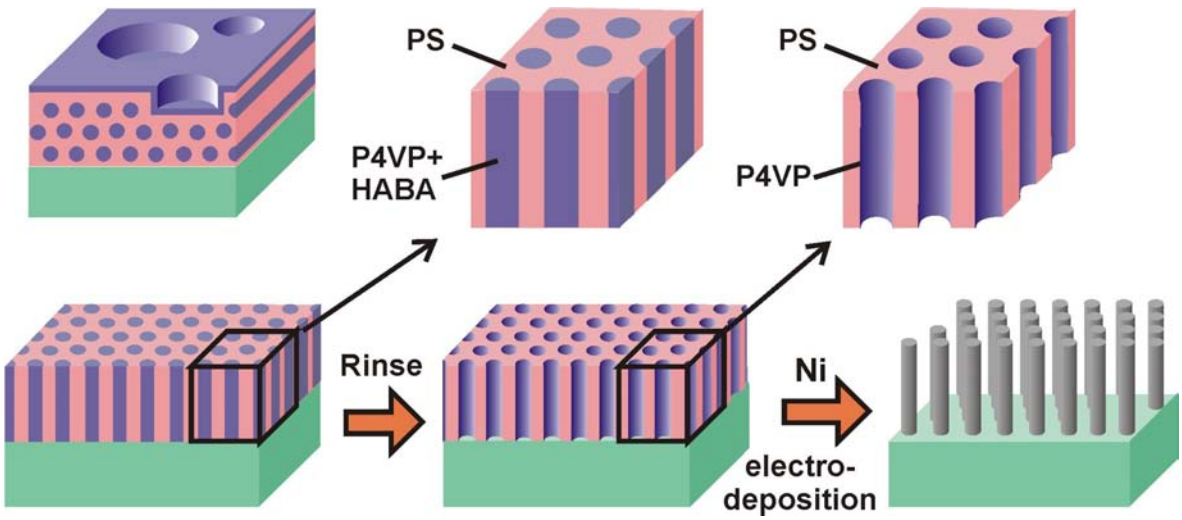


Figure 1. General concept of the use of block copolymer assembly approach for nanotemplating.

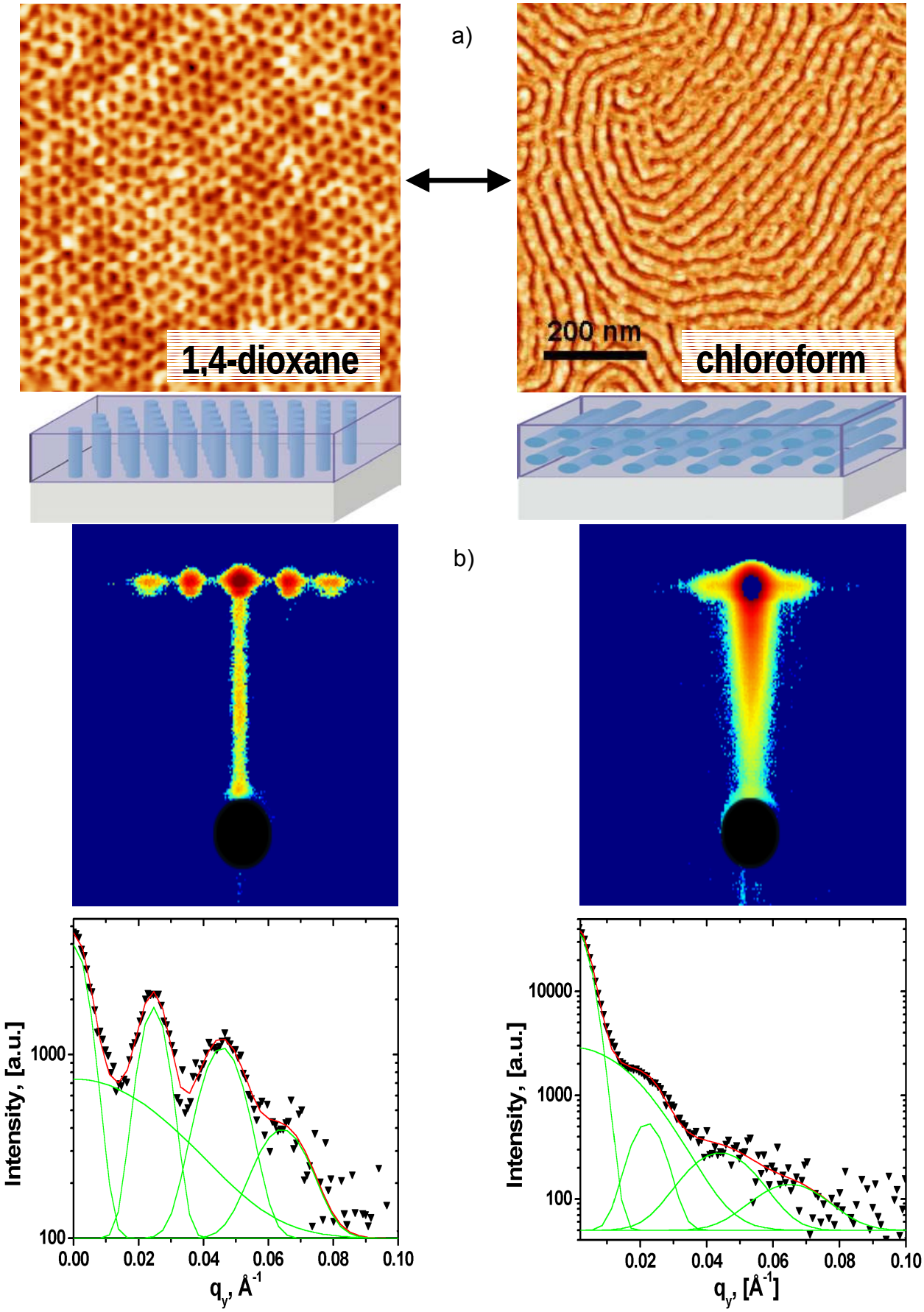


Figure 2. Solvent induced switching of the orientation of cylinder forming BCA as evidenced by AFM (a) and GISAXS (b).

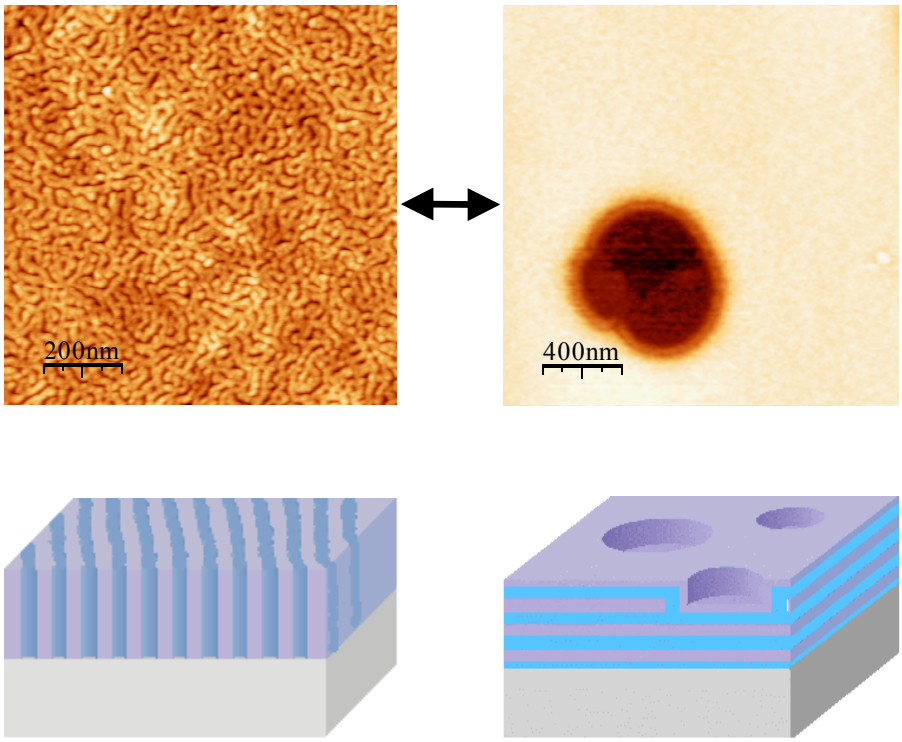
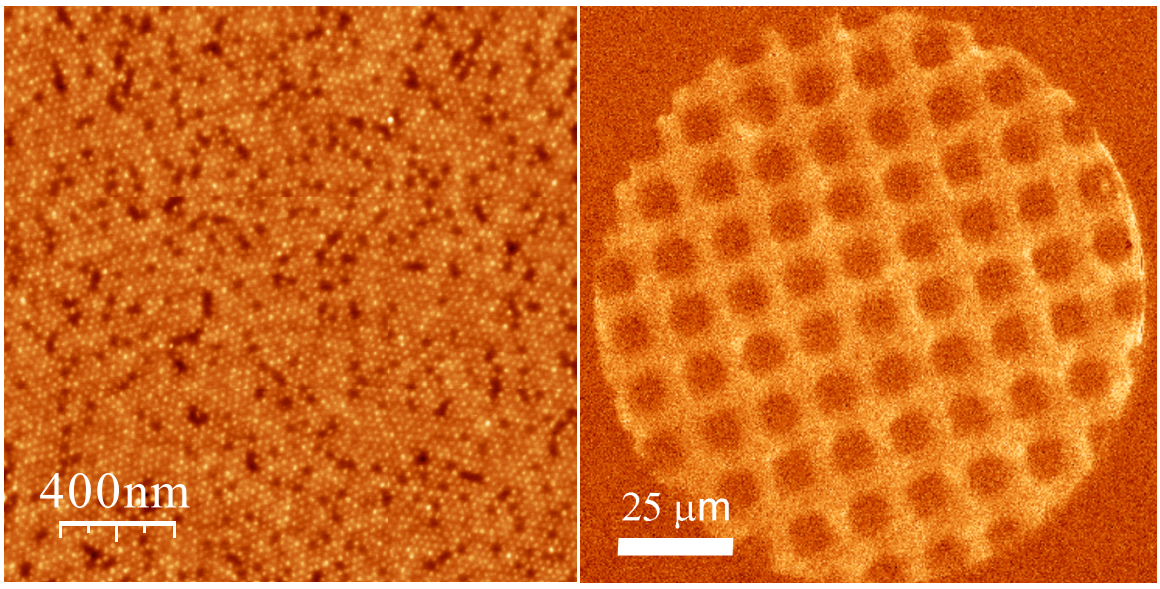


Figure 3. Solvent induced switching of the orientation of lamella forming BCA as evidenced by AFM.



a) b)

Figure 4. Array of Ni dots loaded by electrochemical deposition through BCA nanotemplate (a) and XPEEM images at Ni2p peak of hierarchically ordered Ni array (b).

Estimation of applicability of the obtained results.

The results obtained in the frame of the project are of sufficient interest for both fundamental science and applications. We have synthesized a novel class of materials with unique properties, i.e. block copolymer supramolecular assemblies and investigated their properties, such as selective formation of hydrogen bonds, microphase separation in bulk and in thin films, and the fine structure of the BCAs. Moreover, we described a new phenomenon of solvent induced orientation and switching in thin films of BCAs. We expect that this results might give an impulse to further fundamental investigations in this field.

The obtained results open a venue to fabricate polymer nanotemplates with ordered channels of nanometer scale periodicity. We demonstrated that loading of the nanotemplates with functional species allows to obtain well-defined periodic arrays of nanodots / nanowires with specific properties. It is a subject of the further investigations to improve the loading procedures in respect to the quality of the nanoarrays and evaluate the impact of the nanometer feature size on the physical properties of the arrays. The results are of essential interest for number of applications, such as nanotechnology, photonics, optoelectronics and others.

Use of large instrumentation in the frame of the project

- Beamline BW4 at Hamburg Synchrotron Radiation Laboratory (HASYLAB), Deutsches Elektronen-Synchrotron (DESY)
- U49/2-PGM2 beam line at the BESSY-II (Berliner Elektronenspeicherring-Gesellschaft für Synchrotron Strahlung m. b. H.)

Schlussbericht - Veröffentlichungen

Zuwendungsempfänger: ***Institut für Polymerforschung Dresden e.V. (IPF)***

Projektleitung: ***Prof. Dr. Manfred Stamm***

Charakterisierung und Optimierung von Nano-Templaten aus Polymeren

a) Patent:

"Method for Producing Nanostructured Surfaces and Thin Films" ***WO 03/101628 A1, 2003.***

b) Papers:

1. Sidorenko, A., Tokarev, I., Minko, S., Stamm M. Ordered Reactive Nanomembranes/ Nanotemplates from Thin Films of Block Copolymer Supramolecular Assembly. *J. Am. Chem. Soc*. **2003**, *125*, 12211-12216.

2. Stamm M., Minko, S., Tokarev, I., Fahmi, A., Usov, D. Nanostructures and Functionalities in Polymer Thin Films. Accepted to *Macromol. Symp.* **2003**.

3. Sidorenko, A.; Tokarev, I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Minko, S.; Stamm, M. "Generation of Nanostructured Materials from Thin Films of Block Copolymer Assembles" in: *Nanostructured Materials***.** Hans-Jörg Fecht (Editor). Wiley InterScience, ISBN: 3-527-31009-**6. August 2004**.

4. Tokarev I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Sidorenko, A.; Minko, S; Stamm, M. Microphase separation in thin films of poly(styrene-block-4-vinylpyridine) copolymer – 2-(4'-hydroxybenzeneazo)benzoic acid assembly. *Macromolecules, **2004*** submitted.

5. Krenek, R.; Sidorenko, A.; Cimrova, V.; Stamm, M. Loading of Reactive Nanomembranes/ Nanotemplates from Block Copolymer Supramolecular Assembly with optically active additives. *Nanoletters*, **2004**, in preparation.

6. Sidorenko, A.; Tokarev, I.; Stamm, M. Switching and fine structure of symmetric block copolymer supramolecular assembly. *Langmuir*, **2004**, in preparartion.

c) Presentations at conferences

1. Tokarev, I.; Sidorenko, A.; Motornov, M.; Minko, S.; Stamm, M. Nanoporous Membranes and Patterned Surfaces from Block Copolymers. *SMARTON 5 Workshop ,Functional Surfaces and Materials. Exploring the Vectorial World',* Kasteel Vaeshartelt Maastricht, The Netherlands, November 15-18, 2001.

2. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Nanotemplates and nanoporous membranes from block copolymers. *66th Früjahrstagung der DPhG,* Regensburg, March 10-15, 2002.

3. Tokarev, I.; Minko, S.; Stamm, M. “Hairy Tube" Polymer Templates From Diblock Copolymer Thin Films. *American Material Research Society Spring Meeting,* San Francisco, USA, April 2-4, 2002.

4. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Organized array of metallic nanoclusters via self-organization of block-copolymers. *International Workshop on Nanostructures for Electronics and Optics (NEOP)*, Dresden, October 6-9, 2002.

5. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Nanotemplates from block copolymers for fabrication of regular arrays of nanowires and nanodots. *Discussion Meeting on Multi-level Ordering ‘Molecular Organization for Nanosystems’*, Kloster Banz, February 15-20, 2003.

6. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Nanotemplates based on block copolymer assembles. *67th Frühjahrstagung der DPhG*, Dresden, March 24-28, 2003.

7. Křenek, R.; Sidorenko, A.; Cimrová, V.; Minko, S.; Stamm, M. Optical properties of photoactive materials prepared via polymeric templates. International Polymer Seminar. Gliwice, Poland 03.07.03

8. Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. Ordered Nanotemplates from Thin Films of Block Copolymer Assembles. European Congress on Advanced Materials and Processes. 1-5 September 2003. Lausanne, Switzerland.

9. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Novel Supramolecular Approach to Periodic Nanostrucutres in Thin Polymer Films. 226th ACS National Meeting. September 7-11, 2003. New York City, NY.

10. Sidorenko, A.; Krenek, R.; Minko, S.; Stamm, M. Ordered Arrays of Photoswitchable Nanodomains from Thin Films of Block Copolymer Supramolecular Assembles. 226th ACS National Meeting. September 7-11, 2003. New York City, NY.

11. Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. Switching nanotemplates. 227th ACS National Meeting. March 27 - April 1, 2004. Anaheim, CA.

d) PhD thesis

I. Tokarev, **Order in Thin Films of Diblock Copolymers by Supramolecular Assembly**, Dissertation, Technische Universität Dresden (2004)