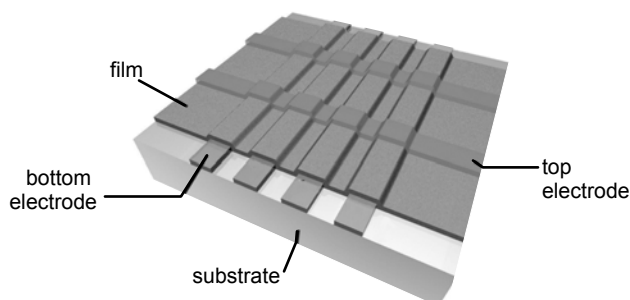


Block copolymer nanotemplates with optically active low-molar-mass additives

Die Selbstorganisation von Blockcopolymeren kann zur Herstellung von geordneten, dünnen Nanotemplat-Filmen verwendet werden, die für optische oder mikroelektronische Anwendungen interessant sind. Wir berichten hier, neben anderen Arten der Funktionalisierung, vorrangig über die Mischung von Poly(styren-block-4-vinylpyridin) mit verschiedenen optisch aktiven Zusätzen. Zunächst beschreiben wir die Herstellung der Nanotemplate und zeigen ihre potentiellen Anwendungen auf. Der Hauptteil des Berichts befasst sich mit den Zusammenhängen von Wasserstoffbrückenbindungen, Mischungsverhältnis und Lösungsmitteldampftemperatur auf der einen Seite und der Oberflächenbeschaffenheit der porösen Nanotemplate auf der anderen Seite. Wir erklären die Einzigartigkeit von 2-(4-Hydroxyphenyl-azo)-benzoesäure als Volumenadditiv, welches, durch die günstige Position der Carboxyl- und Hydroxylgruppe und die damit verbundene Stabilisierung des Moleküls im Aggregat, hochgeordnete Nanotemplate erzeugt. Einige Beispiele von Nanotemplaten mit optisch aktiven niedermolekularen Zusätzen, welche in den dünnen Filmen zur Aggregation neigen, werden ebenfalls vorgestellt. Wir beschreiben bestimmte Effekte, die aus dieser Aggregatbildung folgen. Abschließend zeigen wir Mischungs- und Lösungsmiteleinflüsse auf makroskopischer Ebene Nanotemplate mit dem Fluoreszinderivat 5(6)-Carboxy-fluoreszin. Anhand dieser Proben wiesen wir Zusammenhänge zwischen strukturellen Parametern, Absorption und Fluoreszenz nach.

Introduction

Nanotemplates are thin film matrices developed via self-assembly of atomic and molecular moieties. They represent the bottom-up approach of nanolithography which affords cheap fabrication of ordered nanostructures with characteristic dimension of about 10 nm. Nanotemplates can be deposited on a bit larger structures (e.g. electrodes, Fig. 1) developed via the top-down approach in order to build-up a final product like light emitting diode (LED), photovoltaic (PV) cell, or storage disk [1, 2]. Scaling-down of the structures brings more efficient physical properties to the devices. For instance, enhanced electron-photon conversion may be achieved thanks to superior heterogeneity of nanotemplates (high interface) in contrast to conventional microdevices. The purpose of miniaturization is very apparent in shrinking of unit records in storage media.



Keywords

nanotemplates
hydrogen bonding
blends
fluorescence

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Fig. 1:

Top-down and bottom-up lithographic processes are useful e.g. for development of displays which consist of arrays of light emitting diodes. Electrodes may be prepared via a top-down approach (like photolithography) and the nanoscale heterogeneity of the film can be achieved via bottom-up microphase separation of a block copolymer.

Nanotemplates can be both inorganic and organic, respectively. The most known inorganic nanotemplates are anodized from high-purity aluminum foils [3]. Alumina nanotemplates feature predominantly by high anisotropy, which is useful for both optical and magnetic application. On the other hand, thin film alumina masks may be prepared via step anodization combined with poly(methyl methacrylate) (PMMA) template stripping. Organic nanotemplates are mostly based on linear block copolymers which may be further categorized according to incompatibility of their blocks. For instance, amphiphilic block copolymers are almost ideally incompatible, therefore, they micellize in very polar, or apolar solvents [4]. Formation of spherical or cylindrical micelles is mostly used for ordering of composite nanodots in thin films in hexagonal arrays [5].

Generally, strongly incompatible blocks undergo microphase separation and need not be amphiphilic (e.g. poly(styrene-*block*-4-vinylpyridine), poly(styrene-*block*-methyl methacrylate), etc.). These blocks are microphase separated in well-defined micro-domains of several morphologies (spherical, cylindrical, gyroidal, lamellar), depending on volume fraction of each block, temperature and chemical dissimilarity of the blocks. Orientation of anisotropic morphologies (cylindrical, lamellar) may be controlled by many approaches. They can be summarized in four basic categories – control by thickness, interfacial interaction, external field, and multiple alignment force [6]. In our approach, we focus on nano-templates with namely cylindrical morphology and solvent controlled orientation and order (as flow external field) [7]. This approach is based on blending of reactive poly(styrene-*block*-4-vinylpyridine) copolymer (PS-P4VP) with the low-molar-mass additive (LMA), 2-(4-hydroxybenzeneazo)benzoic acid (*o*-HABA, from Aldrich). In the original concept, *o*-HABA serves as a temporary volume substituent which can be selectively rinsed from block copolymer in order to develop porous nanotemplates (Fig. 2) [7].

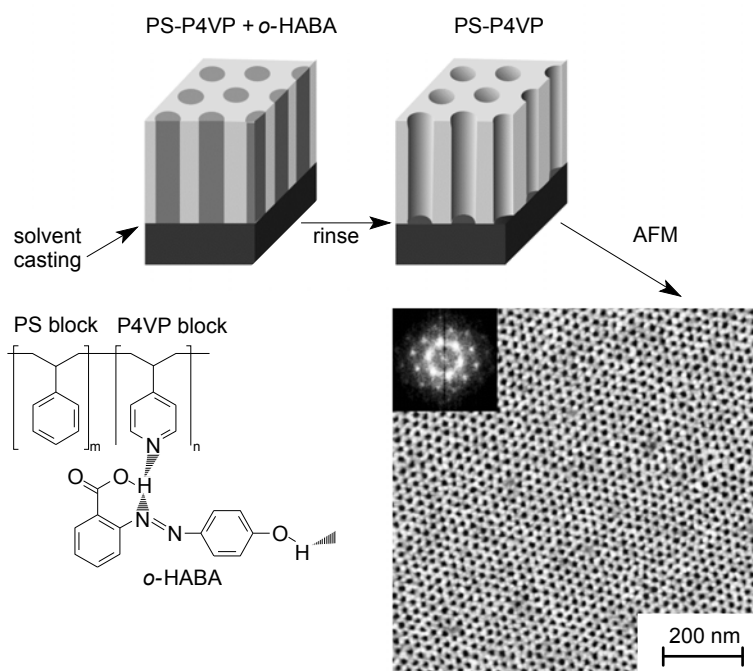


Fig. 2: Schematic development of PS-P4VP nanotemplates. PS-P4VP and *o*-HABA are dissolved in a selective solvent (1,4-dioxane) in equimolar ratio between LMA and 4VP. Nanotemplates are cast e.g. by vertical dipping from 0.5-2.0 % [w/v] solutions which results in 15-80 nm thin films. Characteristic intercore distance is 25 nm.

Anisotropy in the nanotemplates is eminent for optical and magnetic devices. In hierarchical block copolymer nanostructures, it is related with organization of LMA molecules, [8] therefore, polarization (and enhancement) of their spectral characteristics may be observed [9].

Wave-guiding of the light is a further referenced effect [10]. However, it takes place in nanostructures with high aspect ratios which have not been achieved by our approach yet. In magnetism, the magnitude of the magnetic moment is also dependent on the aspect ratio. In this report, we focus namely on formation of nanotemplates with various additives and demonstration of their photoluminescent spectra in respect to solvent annealing.

Hydrogen bonds in nanotemplates

Our approach utilizes hydrogen bonding of PS-P4VP with a LMA in order to give functionality to nanotemplates directly upon deposition from solution. However, it turned out that the choice of additives is limited by several factors. In parallel with *o*-HABA, we tried to develop nanotemplates with 3-pentadecyl phenol (PDP, Sigma) [11], 1-pyrene methanol (PyM, Aldrich), and 4-(phenylazo)benzoic acid (PBA, Aldrich). Their formulae are depicted in Fig. 3. Although heated 1,4-dioxane (at 80 °C) can dissolve all these additives (thanks to thermal dissociation of hydrogen bonds), not all the molecules react with 4VP monomer to create P4VP–LMA complex, upon cooling back to room temperature. The insufficient complexation results in aggregation or crystallization of LMA in the thin film of PS-P4VP–LMA. Appearance of the film depends on the cooling history which has influence on aggregation of LMA. There are several reasons why aggregation takes place with these additives and not with *o*-HABA.

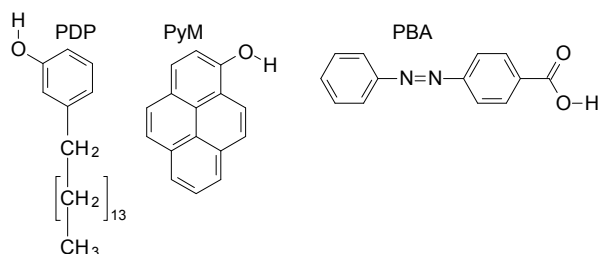


Fig. 3:
Molecular formulae of few LMA which aggregate in nanotemplates: 3-pentadecyl phenol (PDP), 1-pyrene methanol (PyM) and 4-phenylazo-benzoic acid (PBA)

Hydroxyls of PDP and PyM provide weak hydrogen bonding only, which is not sufficient to hold these surfactant molecules in the thin film assembly. Due to planar structure, PyM can then crystallize in the film (Fig. 4). On the other hand, exposed carboxyl of PBA results in dimerization of PBA molecules during cooling. The dimers can again aggregate in the film. In contrast to these additives, intramolecular bonding of the carboxylic group in *o*-HABA prevents HO–C=O...HO–C=O dimerization. Moreover, hydroxyl of *o*-HABA reduces surfactancy of the molecule and can take part in extramolecular bonding in the thin film assembly with PS-P4VP.

In the following, we demonstrate the effect of bonding groups of LMAs on the self-assembly with PS-P4VP. We compare the best additive *o*-HABA with 4-(4-hydroxybenzeneazo)benzoic acid (*p*-HABA, synthesized in the group of Dr. F. Böhme) and N-(4-methoxybenzylidene) anthranilic acid (MBA, from Aldrich). Nanotemplates with these LMAs were prepared from blends with PS-P4VP ($M_{n,PS} = 35,500 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,P4VP} = 3,700 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.06; LMA: 4VP = 1:1) dissolved in 1,4-dioxane at 0.8 % [w/v]. All the films were annealed in vapors of 1,4-dioxane for 65 h.

Fig. 4:
 AFM topography ($2 \times 2 \mu\text{m}^2$) of a PyM aggregate in 30 nm thin nano-
 template developed via self-as-
 sembly with PS-P4VP copolymer
 ($M_{n,PS} = 34,000 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,P4VP} =$
 $2,900 \text{ g}\cdot\text{mol}^{-1}$; $PDI = 1.07$;
 PyM : 4VP = 1:1) from toluene so-
 lution. Both the height (on the left),
 and the phase signal (on the right)
 profile respectively, are taken along
 the lines inscribed in the AFM
 images.

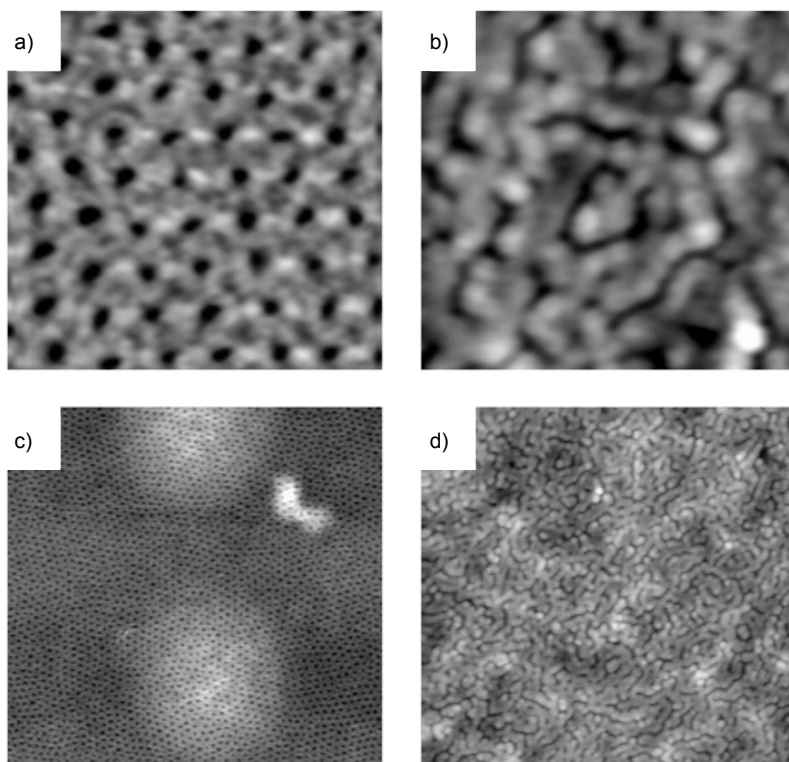
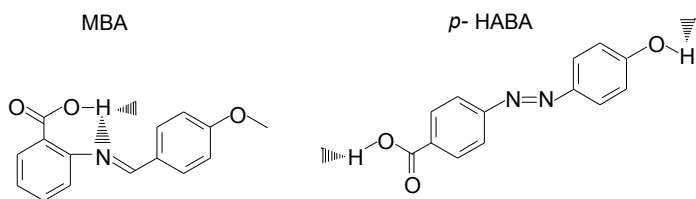
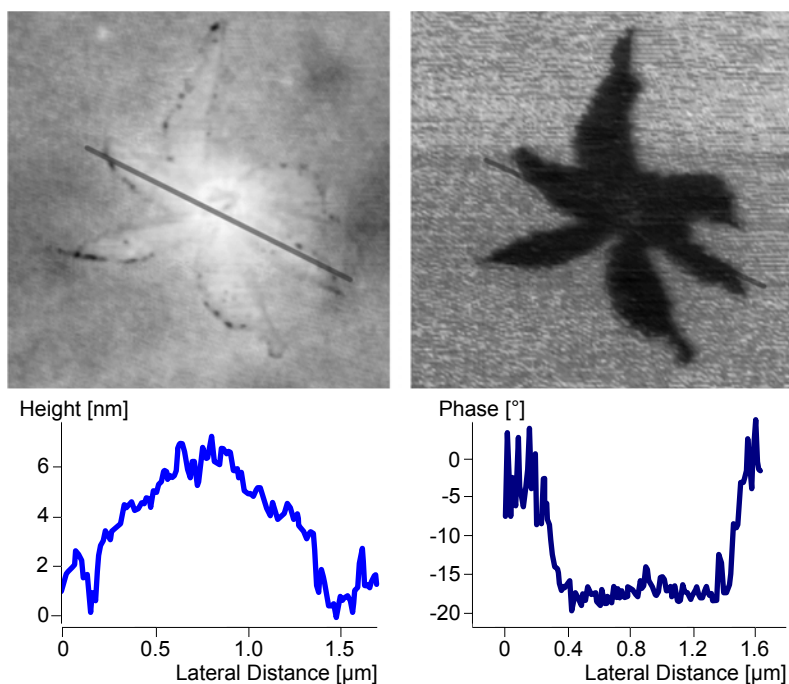


Fig. 5:
 Molecular formulae of LMA that
 resemble with *o*-HABA: *N*-(4-meth-
 oxybenzylidene)anthranilic acid
 (MBA, on the left) and 4-(4'-
 hydroxybenzene azo)benzoic acid
 (*p*-HABA, on the right). AFM topo-
 graphs, which reflect major differ-
 ences with reference to nano-
 templates based on *o*-HABA (Fig.
 2), are presented for following
 lateral scales: (a, b) $200 \times 200 \text{ nm}^2$,
 (c, d) $1.5 \times 1.5 \mu\text{m}^2$.

In Fig. 5, AFM topographies show effect of H-bonding groups of azobenzene (benzylidene) additives on formation of thin film assemblies with PS-P4VP. Evidently the most important is intramolecular H-bonding of the carboxylic group which prevents dimerization of molecules. Nevertheless, the opposite hydroxyl group helps to *stabilize* the molecules in the supramolecular assembly, either via bonding with other molecules of LMA, or with P4VP block, respectively.

The methoxy group of MBA provides only very weak hydrogen bonding, therefore, MBA aggregates locally in the film. Aggregation of MBA is weaker (and sub-microscopic) than in PyM nanotemplates which is distinguished by distinct separation of PyM crystals and the nanotemplate. In summary, complexation through intramolecularly weakened carboxylic group is pretty unique but optically active molecules may be bonded through other hydroxyl groups, which are well-proportioned over the molecule.

Blending ratio and solvent effects on fluorescence

Formation of LMA blended nanotemplates is strongly dependent on the molar ratio between LMA and 4VP unit of P4VP block, as well as on the solvent, which is used for deposition. We demonstrate these effects on 5(6)-carboxyfluorescein (COF, from Fluka). COF in the lactoid configuration (Fig. 6) is a yellow fluorescent dye with absorption (and excitation) at around 450 nm and emission around 550 nm. Dimerization effect in 1,4-dioxane is reduced thanks to well-proportioned hydroxyl groups over the molecule. However, dioxane is not a suitable solvent for development of COF nanotemplates, since COF complexes with P4VP precipitate in it. Therefore, we focused on development of nanotemplates from pyridine, which is very good solvent for all the substances. We prepared blends of COF with P4VP and PS-P4VP in stoichiometric ratio 1:1, 1:2, and 1:3 (COF : 4VP). Ratios 1:1 and 1:2 were prepared with spherical block copolymer ($M_{n,PS} = 34,000 \text{ g}\cdot\text{mol}^{-1}$, $M_{n,P4VP} = 2,900 \text{ g}\cdot\text{mol}^{-1}$, PDI = 1.07), ratio 1:3 was prepared with cylindrical block copolymer ($M_{n,PS} = 40,000 \text{ g}\cdot\text{mol}^{-1}$, $M_{n,P4VP} = 5,600 \text{ g}\cdot\text{mol}^{-1}$, PDI = 1.09). Since COF increases the volume fraction of the minor block (P4VP), morphology of all these blends should be cylindrical. We cast the films from 2 % [w/v] solution by vertical dipping.

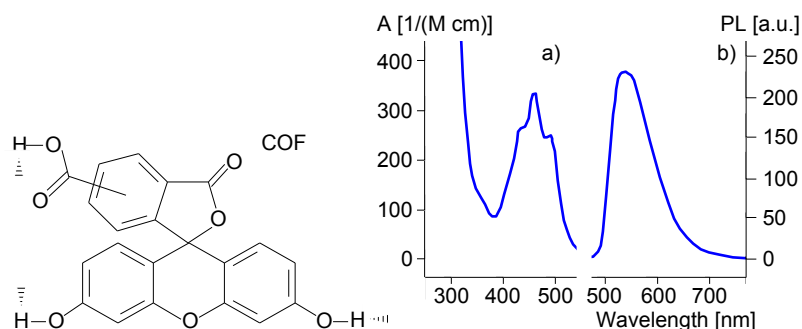
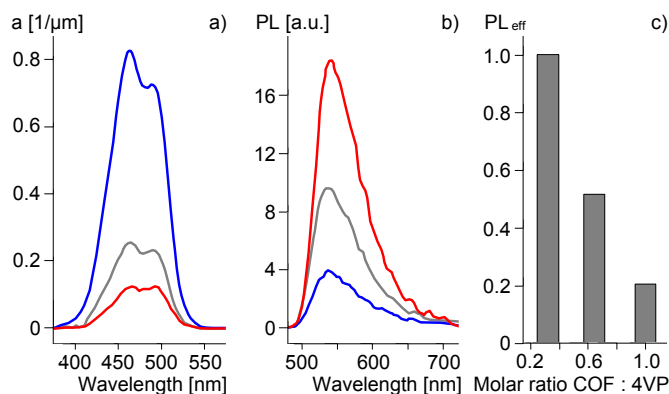


Fig. 6: Molecular formula, and (a) UV-Vis absorption ($A = \text{molar absorptivity}$) and (b) PL emission spectra in pyridine respectively, of 5(6)-carboxyfluorescein (COF). Excitation wavelength was 465 nm.

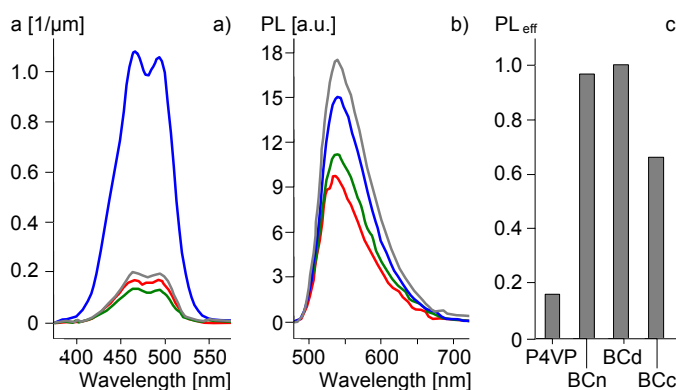
Fig. 7 (a and b) shows absorption and emission spectra of COF blends with PS-P4VP and various blending ratios. Evidently, the most efficient photoluminescence (PL) is obtained in the least concentrated system. This effect was observed many times and was related to quenching due to dimer interaction. PL efficiency of all the COF blends with P4VP and PS-P4VP is depicted as function of blending ratio in Fig. 7c.

Fig. 7: (a) UV-Vis absorption (a = absorption coefficient), (b) PL emission, and (c) relative PL efficiency (PL_{eff}) of COF blends with PS-P4VP. Three molar ratios between COF and 4VP unit of P4VP block are compared: 1:1 (blue line), 1:2 (gray line), and 1:3 (red line). Excitation wavelength was 465 nm.



Likewise, we can evaluate spectra of COF nanotemplates from the viewpoint of orientation of their morphology, which can be achieved by solvent annealing [7, 11]. Fig. 8 (a and b) shows absorption and emission spectra of COF nanotemplates and COF blend with P4VP in ratio 1:3 (COF : 4VP). PL efficiency of the blends is depicted in Fig. 8c. Here, BCn denotes PS-P(4VP + COF) without annealing. BCd, and BCc respectively, were annealed in 1,4-dioxane, and chloroform respectively, for 65 h.

Fig. 8: (a) UV-Vis absorption (a = absorption coefficient), (b) PL emission, and (c) relative PL efficiency (PL_{eff}) of 50 nm films made of blends: COF + P4VP (blue line) and COF + PS-P4VP – BCn without annealing (gray line), BCd annealed in 1,4-dioxane (green line) or BCc annealed in chloroform (red line) vapor. Excitation wavelength was 465 nm.



Topography of these samples upon rinsing in methanol (selective rinsing of COF from nanotemplates) is shown in Fig. 9. The effect of solvent orientation is apparent among BCn, BCd, and BCc. However, their morphology is not as clear as in PS-P(4VP + *o*-HABA). In the 1:3 blends, small amount of LMA added to cylindrical BC leaves the blended morphology rather cylindrical. Although COF molecule is larger than *o*-HABA less amount of COF in nanotemplates may result in smaller pores. Parallel orientation in BCc can be easily developed since chloroform is non-selective for all the components. But perpendicular orientation requires certain selectivity of solvent between PS and P(4VP + LMA) block – as we have shown formerly, it is 1 : 10 for PS-P(4VP + *o*-HABA) [11]. This selectivity depends on interaction of P(4VP + LMA) complex with the solvent used for vapor annealing. Swelling of P(4VP + COF) complex will be a subject of our further investigation.

The blending ratio, demonstrated on BCd, affects the granularity of the surface. Although the granularity is something explicitly observable with AFM, implicit relation with photoluminescence is impacted again through the solvent effects. The granularity comes from violent extraction of COF molecules, bonded to P4VP via carboxyls, during rinsing with methanol. It is reduced with growing concentration, when COF molecules dimerize in pores (Fig. 9 a-c). Dimerized molecules or oligomers are bonded to P4VP via weak hydroxyls and may be rinsed without disruption of the nanotemplate.

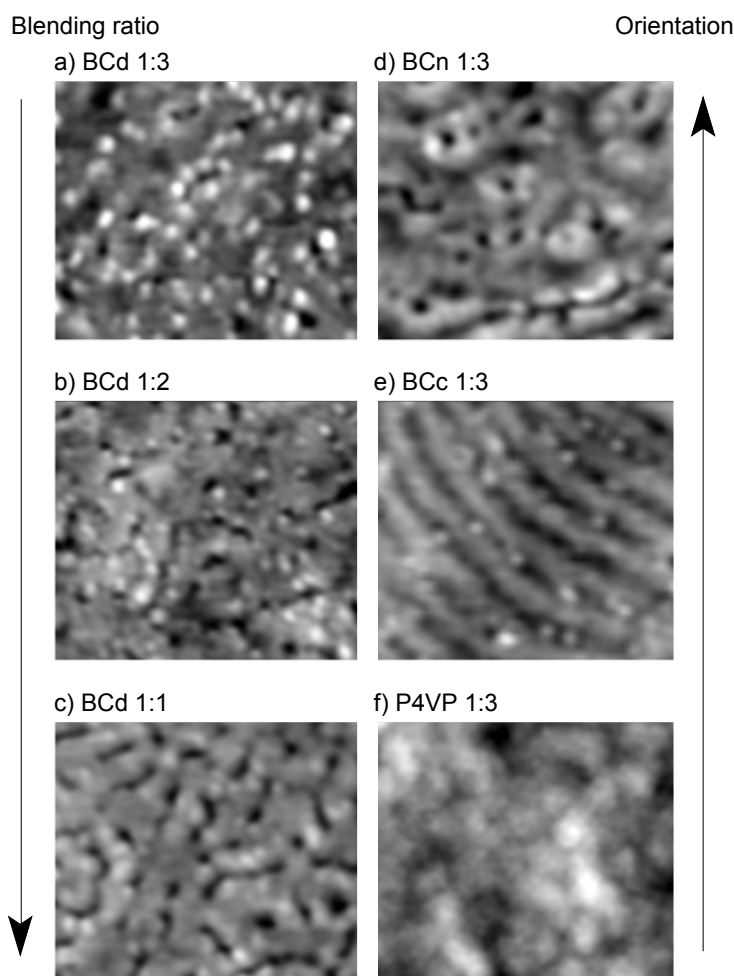


Fig. 9: AFM topography ($250 \times 250 \text{ nm}^2$) of COF thin film blends with PS-P4VP and P4VP in dependence on blending ratio (a, b, c), and orientation of morphology (a, d, e, f), respectively.

In BCn (Fig. 9d), morphology is formed during shrinkage from pyridine. Pyridine is more basic than P4VP, therefore, COF-solvent interaction is preferred over COF-P4VP. As pyridine partial pressure reduces, P4VP substitutes pyridine interactions with COF hydroxyls. Upon shrinkage, COF is bonded to P4VP predominantly via hydroxyls and its carboxyl keeps residual solvent (pyridine) in the pores. Such solvent solidification is not unique for this system only.

The granularity appears namely after dioxane annealing (Fig. 9a). During annealing, dioxane can substitute residual pyridine thanks to its solvation power and partial pressure. With respect to half basicity of dioxane in comparison with pyridine [12], COF carboxyls prefer interaction with P4VP than dioxane (P4VP is more basic than dioxane) upon shrinkage.

Chloroform has practically null basicity, therefore, it bonds rather to P4VP than COF during annealing. Meanwhile, its partial pressure can push pyridine out. COF carboxyls do not interact with chloroform (null basicity) and dimerize because P4VP is mostly occupied by excess of chloroform. Consequently, we can see less granular surface than in case of dioxane annealing (Fig. 9e). Some extent of granularity is present due to fractional interaction of COF carboxyls with P4VP.

Besides the presented approach of direct blending, we developed also a method for soaking of porous nanotemplates in LMA solutions [13], thanks to stabilization of nanotemplates by UV irradiation [14]. With respect to opto-electronic applications, we studied thoroughly DC charge transport and formation of PS-P4VP nanotemplates on various electrodes [15].

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