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Nucleation and Growth of TiO_2 Thin Films on Modified Polystyrene Surfaces

Anke Dutschke, Carsten Diegelmann, and Peer Löbmann*

Lehrstuhl für Silicatchemie, Universität Würzburg, Röntgenring 11, D-97070 Würzburg, Germany

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Partially crystalline TiO_2 was deposited on polystyrene substrates by liquid phase deposition. Both nucleation and adhesion depend on the respective pretreatment of the polymer. Coherent films are formed on untreated substrates and surfaces hydroxylated by aqueous sodium peroxodisulfate solution, but satisfactory film adhesion is only observed on the modified surface. The formation of continuous films is not observed on polystyrene etched by H_2SO_4/SO_3 where material deposition was only initiated at few nucleation sites. The TiO_2 precipitation was characterized as a function of time and compared to previous results on wet chemically grafted PS. A film formation mechanism is proposed which can account for the textured constitution of TiO_2 observed by X-ray diffraction experiments.

1. Introduction

For the coating of polymer surfaces with inorganic thin films mostly methods such as plasma-enhanced chemical-vapor deposition (PE-CVD)[1] or sputtering[2] are applied. Even though wet chemical processing methods generally require considerably lower equipment costs than vacuum-based technologies, the temperatures required to anneal as-deposited sol−gel films generally do not allow the coating of sensitive organic polymers with crystalline ceramic materials.

New approaches for polymer coating have been inspired by biomineralization processes,[3−4] where inorganic materials are obtained under physiological conditions at ambient temperature.[5] In living organisms the material deposition from supersaturated solutions presumably is induced at specific surface groups within supramolecular scaffolds: iron-oxo-hydroxides, for example, selectively nucleate at neighboring −COOH moieties within the protein cage of ferritin.[6]

Synthetic surfaces with high densities of functional groups such as Langmuir films[7,8] and self-assembled monolayers (SAMs)[9−11] have been utilized for thin film formation mimicking these natural processes of biomineralization. To transfer the general concept to temperature-sensitive substrates with a broader technical applicability, polystyrene surfaces have been modified by wet chemical grafting and subsequently were exposed to solutions supersaturated with respect to TiO_2.[12] TiO_2 with an estimated crystallinity of 58% was formed by this liquid phase deposition method on both functionalized and untreated polymer. In contrast to the unmodified surface, a thin coherent inorganic film is formed on polystyrene grafted with 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) in the early stage of mineralization. Whereas the inorganic material readily delaminates from the untreated polymer, a significantly improved adhesion is observed on the functionalized surface.

Because grafting reactions are commonly induced by plasma activation, the biologically inspired mineralization described above includes a vacuum processing step. To achieve practical advantages over well-established techniques, simpler surface functionalization reactions have to be employed. In this paper we describe the surface treatment of polystyrene by wet etching and wet chemical hydroxylation. The subsequent liquid phase deposition (LPD) of TiO_2 on such surfaces has been studied as a function of time and compared with results on AMPS-grafted substrates.

2. Experimental Procedure

2.1. Polymer Surface Modification. Polystyrene substrates ($25 \times 75 \times 1.2$ mm^3) were purchased from Goodfellow Ltd. and ultrasonically cleaned in succession with an aqueous detergent solution (Ultrasonol7, Roth), ethanol (Roth, 99.8%), and deionized water.

Polymers were hydroxylated by an aqueous sodium peroxodisulfate solution (15 mass %, Fluka) at 80 °C for 60 min.

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* Corresponding author. Phone: +49 (0)931 31 26 31. Fax: +49 (0)931 31 21 09.E-mail: loebmann@silchem.uni-wuerzburg.de.

[1] Martinu, L.; Poitras, D. *J. Vac. Sci. Technol. A* **2000**, *18*, 2619.

[2] Herrero, J.; Guillen, C. *Vacuum* **2002**, *67*, 611.

[3] Baeuerlein, E., Ed. *Biomineralization: From Biology to Biotechnology and Medical Application*; Wiley-VCH: New York/Weinheim, 2000.

[4] Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*; Oxford University Press: New York, 2001.

[5] Mann, S. *Biomimetic Materials Chemistry;* VCH: New York, 1996.

[6] Chasteen, D.; Harrison, P. *J. Struct. Biol.* **1999**, *126*, 182.

[7] Heywood, B.; Mann, S. *Adv. Mater.* **1994**, *6*, 9.

[8] Calvert, P.; Rieke, P. *Chem. Mater.* **1996**, *8*, 1715.

[9] Agarwal, M.; DeGuire, M.; Heuer, A. *J. Am. Ceram. Soc.* **1997**, *80*, 2967.

[10] DeGuire, M.; Niesen, T.; Supothina, S.; Wolff, J.; Bill, J.; Sukenik, C.; Aldinger, F.; Heuer, A.; Rühle, M. *Z. Metallkd.* **1998**, *89*, 758.

[11] Niesen, T.; DeGuire, M.; Bill, J.; Aldinger, F.; Rühle, M.; Fischer, A.; Jentoft, F.; Schlögl, R. *J. Mater. Res.* **1999**, *14*, 2464.

[12] Dutschke, A.; Diegelmann, C.; Löbmann, P. *J. Mater. Chem.* **2003**, *13*, 1058.

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Surfaces were etched by immersion of substrates in 98% H_2SO_4/SO_3 solution (fuming sulfuric acid, 20% SO_3, Riedel-de-Haen) for 1 s and immediately rinsed to prevent extensive decomposition of the polymer. After wet chemical surface modification and rinsing, the substrates were dried with compressed air and immediately used for measurements or mineralization experiments.

The surface modification of polystyrene by plasma activation and subsequent radical grafting with 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) is described elsewhere.[12]

2.2. TiO_2 Film Deposition. The LPD procedure employed was adopted from Koumoto et al.[13] Ammoniumhexafluorotitanate (AHFT, 0.98 g (0.005 mol), Aldrich 99.99%) was dissolved in 70 mL of deionized water and mixed with 30 mL of a 0.5 M boric acid (Fluka, 99%, purum p.a.) stock solution to form a solution containing 0.05 M AHFT and 0.15 M boric acid. By adding 2 M HCl (Merck, p.a.) the pH was adjusted to 2.8 without significantly increasing the solution volume.

The respective substrates were vertically immersed into freshly prepared deposition solutions at 50 °C. After various deposition times any weakly adherent material was removed from the coated substrates by intensive rinsing with water and subsequent drying with compressed air.

2.3. Material Characterization. Contact angles (water, 5 μL) were measured automatically with a dataphysics ACA50 for 10 s after setting the drop. To investigate the surface morphology of the pretreated substrates and the deposited material, atomic force microscopy (AFM) images were obtained in an autoprobe M5 in the noncontact mode.

The microstructure of the deposits was characterized by transmission electron microscopy (TEM) using a Phillips CM12 STEM with an accelerating voltage of 120 kV. For this purpose cross-sections showing the interface between the films and the polystyrene substrates were prepared by ultramicrotomy using a Reichert OmU2. The chemical composition of the samples was determined by energy-dispersive X-ray analysis using an EDAX 9900 detector system. Crystalline phases were identified by selected area electron diffraction (SAED) and convergent beam electron diffraction (CBED).

To evaluate the film adhesion, the coated samples were treated with a sharp water jet; poorly adhering films were removed by this procedure. Samples not damaged by this procedure could be manipulated with tweezers or bare hands without any delamination. These results were confirmed by microscopic characterization of reproducible indentions, details about this procedure were reported elsewhere.[12]

Further surface characterization was carried out by scanning electron microscopy (SEM; Hitachi S 800, field emission scanning electron microscope with SE-detector). Film thicknesses were determined at fractured surfaces.

Grazing incidence X-ray diffractometry (GI-XRD) was carried out using a Siemens D 5005 diffractometer with an angle of incidence of 1°.

3. Results and Discussion

3.1. Polymer Surface Modification. Before film deposition the effect of the different surface modification procedures on the polystyrene substrates was evaluated. In Figure 1 the wetting angle of water is given as a function of time after the respective treatments.

Directly after both processes, etching with H_2SO_4/SO_3 and plasma-activated grafting with AMPS monomers, the contact angle to water droplets is decreased to 30° compared to a value of 90° for unmodified polystyrene. Within 48 h after treatment these values increased to 60° and 45°, respectively, indicating either surface reorganization of the modified polymer or degradation of unstable polar functionalities.[14] By hydroxylation the wetting angle of polystyrene was only lowered to 50° and increased again to 70° with time.

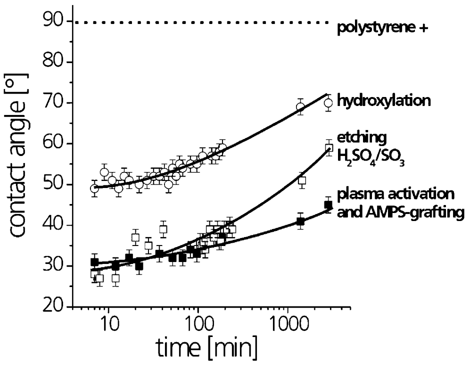

Figure 1. Wetting angles of water with polystyrene surfaces as a function of time after hydroxylation with sodium peroxodisulfate (○), etching with fuming sulfuric acid (□) and plasma-activated grafting with AMPS (■). The contact angle of untreated polystyrene (90°) is given for reference as a solid line, other lines are drawn as guide to the eyes.

For all methods applied, a pronounced surface modification of the polymer within the time frame of the later film deposition experiments can be anticipated, even though the relaxation phenomena will be different for the measured samples stored in ambient atmosphere and substrates immediately exposed to aqueous TiO_2–LPD solutions. The strongest and most lasting increase in surface hydrophilicity is caused by grafting of polar monomers containing $-SO_3H$ groups to the polystyrene, whereas the introduction of less bulky moieties, which is to be expected from hydroxylation and etching, seems to be either less effective or less persistent.

Before the hydrophilicity of the samples can be correlated to the results of film deposition experiments, the changes of the surface topography by the respective modification procedures have to be characterized. In Figure 2 the AFM profiles of the different samples under investigation are given. The linear crosswise structures on the as-cleaned surface were attributed to the indendation of scratches from polished steel rollers during the extrusion of the polymer sheets.[15] Qualitative changes are not introduced by either plasma-activated grafting or oxidative hydroxylation, and only a minor but significant decrease in surface roughness is detected by AFM. Therefore, the increase of hydrophilicity of these samples (Figure 1) should be solely attributed to the formation of polar functional groups. In contrast to this, the topography is strongly altered by etching with H_2SO_4/SO_3 (Figure 2d). The polymer surface is heavily corroded, and bulging protrusions and etch-pits in the lengthscale of several μm led to a significantly increased surface roughness.

3.2. TiO_2 Deposition on Polymer Surfaces. The samples etched with fuming sulfuric acid were exposed to TiO_2 LPD solutions; in Figure 3 SEM images are given after 3 h and 7 h mineralization time. The surface damage resulting from the etching procedure is also detected by electron microscopy. Hemispherical deposits which emerge from the roughened surface after 3 h of

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(13) Koumoto, K.; Seo, S.; Sugiyama, T.; Seo, W. *Chem. Mater.* **1999**, *11*, 2305.

(14) Gupta, B.; Hilborn, J.; Bisson, I.; Frey, P. *PolymerPreprints* **2000**, *41*, 1040.

(15) Beaucage, G.; Marti, O.; Döring, A. personal communications.

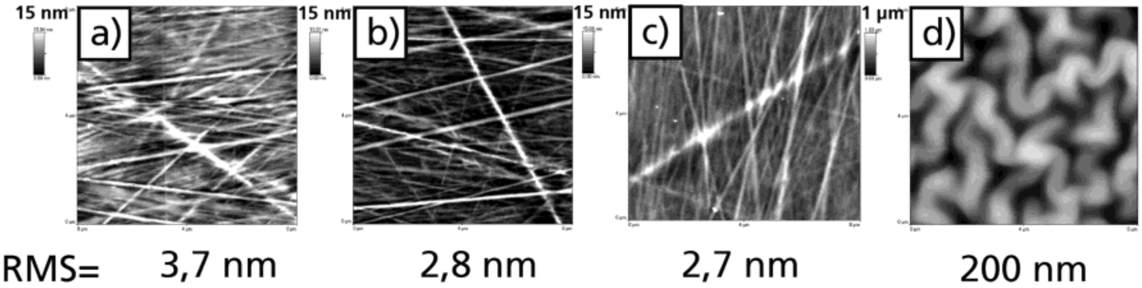

Figure 2. AFM surface profiles of polystyrene samples (8 µm × 8 µm) (a) as cleaned; (b) grafted with AMPS; (c) hydroxylated with sodium peroxodisulfate, and (d) etched with fuming sulfuric acid. The gray scales indicate height resolutions of 15 nm for profiles a–c and 1 µm for profile d. Root-mean-square (RMS) roughness values calculated from the respective measurements are given.

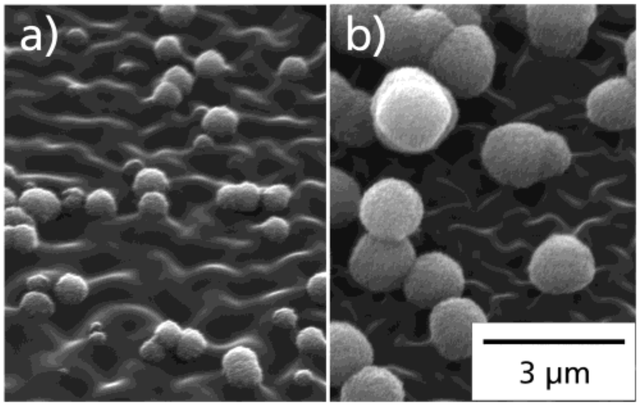

Figure 3. SEM images of polystyrene surfaces etched with H_2SO_4/SO_3 after (a) 3 h and (b) 7 h immersion in a TiO_2 LPD solution.

liquid phase deposition contain Ti as confirmed by EDX measurements. After 7 h the density of nucleation sites had not increased significantly but spherical growth of the deposits is observed. Even though material deposition by a heterogeneous mechanism is always accompanied by homogeneous precipitation in solution, most of the particles in Figure 3b originate from surface nucleation, as a hemispherical shape is a common feature of the deposits. Moreover, spherical particles from solution are effectively removed from the surface by the rinsing procedure after the mineralization.

In contrast to this, the formation of coherent films is observed on hydroxylated polystyrene, samples grafted with AMPS, and even on untreated surfaces. It is important to note that in the case of polystyrene there is obviously no straightforward relationship between surface hydrophilicity and the respective nucleation of TiO_2 and subsequent film formation.

Typical examples of films that had been mechanically removed from the polymer for film thickness determination by SEM are shown in Figure 4. After 5 h, films with an average thickness of 450 nm have mineralized on untreated polystyrene; one surface of the fragments exhibits considerable roughness whereas the bottom of the films that previously had been in contact with the polymer is smooth. After 9 h and growth to approximately 950 nm it is more difficult to distinguish the film sides by their respective roughness, but at some sites large particles (that obviously have been incorporated from the solution) can be identified at the outer surface of the films (Figure 4b). The spherical shape of these precipitates resembles the morphology of the deposits that were found on etched polystyrene in Figure 3. Therefore, it can be concluded that particles homogeneously precipitated in solution and material emerging from single nucleation sites grow by the same mechanism.

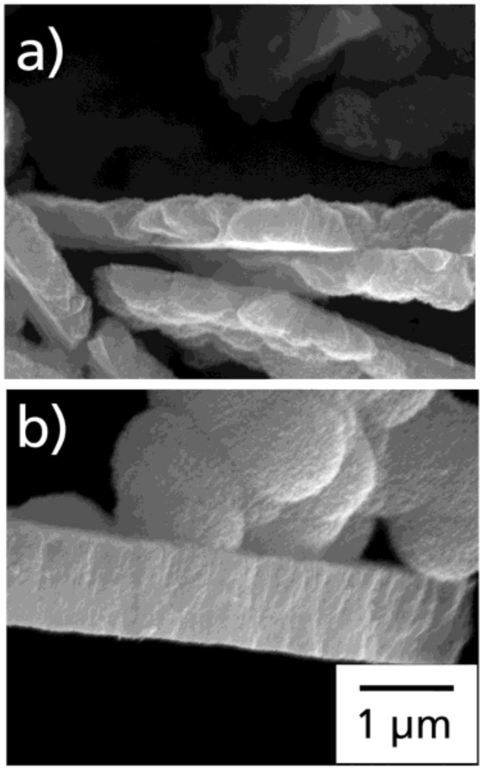

Figure 4. Film fragments mechanically removed from untreated polystyrene surfaces after (a) 5 h and (b) 9 h immersion in a TiO_2 LPD solution.

The assumption of an identical growth mechanism for spherical precipitates and films is further supported by the quantitative analysis of material deposition. For continuous films formed on untreated, grafted, and hydroxylated polystyrene, growth rates between 65 and 100 nm/hour can be estimated (Figure 5). The radial growth of the spherical deposits that were found on surfaces etched with H_2SO_4/SO_3 is in good agreement with these rates.

We previously reported that AMPS grafted polystyrene is already covered with a fine, granular deposit after 5 min of LPD as detected by AFM.[12] TEM imaging revealed that after 15 min a continuous film of 20–40-nm thickness is formed, which is roughly in

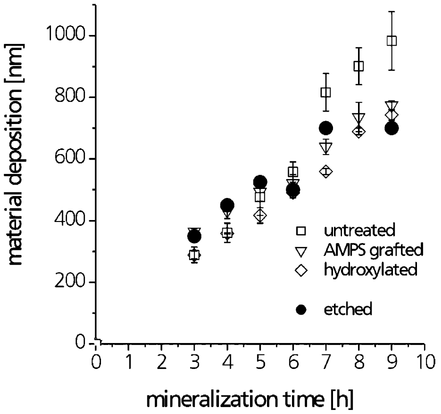

Figure 5. Material deposition by TiO_2 LPD as a function of mineralization time on different polystyrene surfaces. For untreated substrates (□), AMPS-grafted surfaces (▽), and hydroxylated polymer (◇) the film thickness was measured by SEM; for samples etched with H_2SO_4/SO_3 the radius of the spherical deposits (see Figure 3) is given (●).

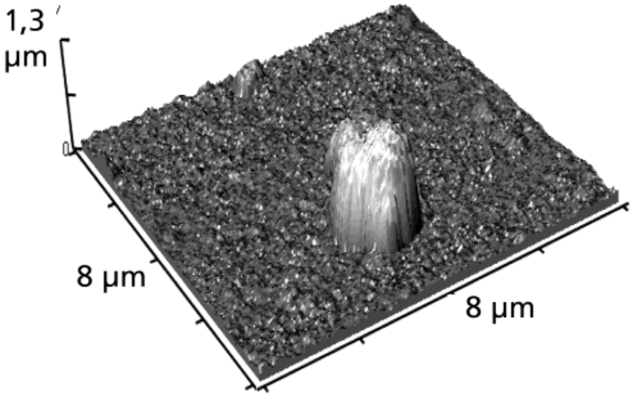

Figure 6. 3-Dimensional AFM surface contour plot (total area 8 μm × 8 μm) of AMPS-grafted polystyrene after 3 h of TiO_2 liquid phase deposition.

agreement with the film growth rate of approximately 85 nm/hour determined for these samples. Larger TiO_2 grains were embedded in this layer.

Even though AFM imaging becomes increasingly difficult with mineralization time, due to the incorporation of larger precipitates from solution, it was possible to take a surface profile of an AMPS-grafted sample after 3 h of liquid phase deposition (Figure 6). The film exhibits a roughness similar to that observed after significantly shorter mineralization times. At single locations larger grains protrude from the rough surface.

Different results are obtained for hydroxylated samples after identical duration of the mineralization (Figure 7). The surface is covered with interconnected granular deposits (designated **1** on the figure) which are similar in shape and size to the material found on etched polystyrene after 3 h. The surface roughness of the single grains is in a comparable order of magnitude as the roughness of films formed on AMPS-grafted polystyrene (Figure 6). The substrate surface, however, is not fully covered, as distinct voids (**2**) are localized within the particulate layer. Again, at single positions (**3**) higher protrusions emerge from the surface due to the aggregation of particles as already observed in Figure 6.

Taking into account the hemispherical material growth, which was observed on etched substrates (Figure 3), an identical mechanism with higher density of nucleation sites can be assumed for the formation of TiO_2 films on hydroxylated polystyrene. After 3 h mineralization time the interstices between the grains are not yet completely filled by radial growth and the adhesion of larger particles homogeneously precipitated in solution starts to contribute to the material deposition.

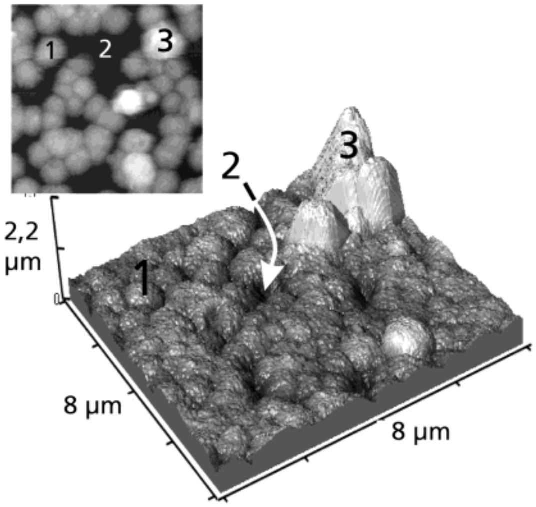

Figure 7. 3-Dimensional AFM surface contour plot (total area 8 μm × 8 μm) of hydroxylated polystyrene after 3 h of TiO_2 liquid phase deposition. A 2-dimensional representation of the same sample area is shown in the inset, and corresponding positions are marked with numbers.

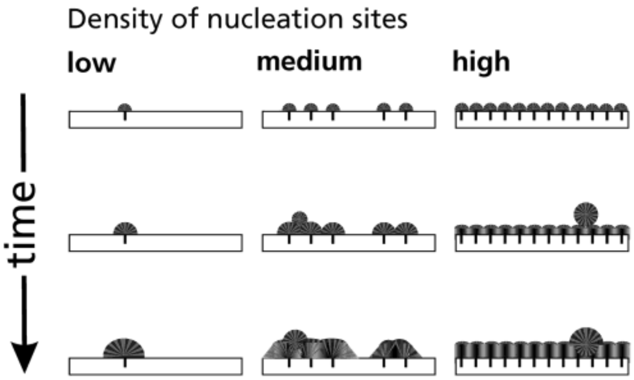

Figure 8. Schematic representation of the mineralization model proposed for the liquid phase deposition of TiO_2 on surfaces with low, medium, and high densities of nucleation sites.

3.3. Film Formation Mechanism. Figure 8 illustrates the mineralization mechanism that can be proposed on the basis of observations of TiO_2 LPD on functionalized polystyrene. On substrates which offer only a low density of nucleation sites, such as polystyrene etched with H_2SO_4/SO_3, hemispherical growth is initiated at only a few locations. The further development of these grains is predominantly undisturbed (Figure 3); their appearance is comparable to deposits homogeneously precipitated in solution that sometimes can be found on other TiO_2 film surfaces (Figure 4b).

The initial mineralization stage is identical on substrates with a higher density of nucleation sites, until neighboring grains are approaching each other (Figure 7). As soon as two deposits get in contact, the horizontal growth is terminated, further material deposition from

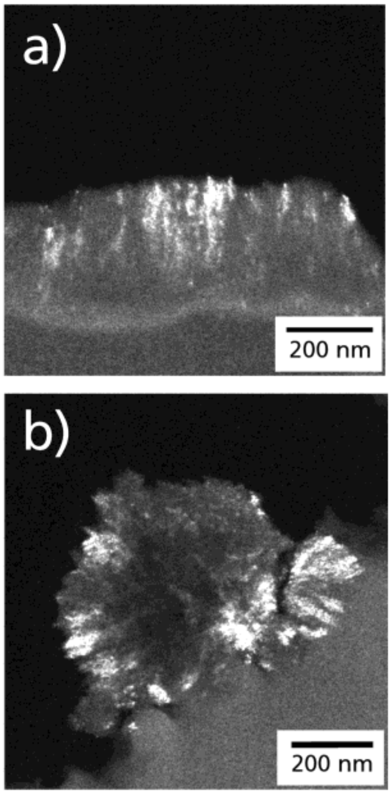

Figure 9. TEM dark field images of (a) TiO_2 film on AMPS-grafted polystyrene after 3 h liquid phase deposition, (b) particulate deposit.

the supersaturated solution can advance only vertically. Nevertheless, between-the-grains mineralization is continued until a continuous film is formed. In the film fragment obtained after 5 h of liquid phase deposition (Figure 4a), the initial granular structure is still visible, whereas after 9 h the film surface is smoother and the cross section suggests a more columnar structure of the material.

If a high density of nucleation sites is provided, the substrates will be covered by small grains at an early stage of mineralization. On polystyrene grafted with AMPS the rapid formation of a granular primer layer was already observed after 5−10 min of LPD.[12] The surface roughness on a small lengthscale remains unaltered (Figure 6); the surface is not as wavy as that observed for samples with underlying larger grains (Figure 7). For optical applications of LPD films high initial densities of nucleation sites thus are advantageous, as structural features with dimensions in the range of the wavelength of visible light will lead to scattering. For the same reason the incorporation of material homogeneously precipitated (Figures 4b, 6, and 7) should be avoided by, e.g., continuous filtering or the exclusive use of freshly prepared LPD solutions.

The proposed model is in agreement with the observation of similar growth rates both for films and solitary particles on etched surfaces (Figure 5), because in all cases the maximum speed is governed by the uniaxial character of the columnar development.

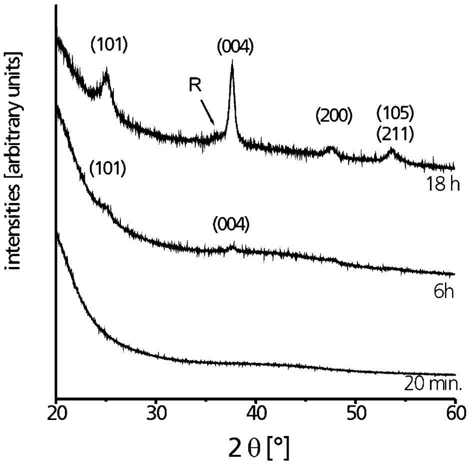

Figure 10. Grazing-incidence X-ray diffraction pattern of TiO_2 films prepared on AMPS-grafted polystyrene after different mineralization times. The respective indices refer to anatase (JCPDS 83 2243). The peak marked as "R" observed after 18 h liquid phase deposition may be attributed to rutile.

To confirm the mineralization mechanism outlined above, TiO_2 deposited on AMPS grafted polystyrene was investigated by transmission electron microscopy (Figure 9a). The film has a thickness of 280−300 nm. As already observed by AFM (Figure 6), the surface is not modulated by underlying grains that emerged from separate nucleation sites (Figure 7). Dark field imaging reveals that the film contains nanocrystalline material which, to some extent, is aligned in columns perpendicular to the substrate. Previous studies indicated that the as-deposited material consists of 60% anatase with crystallite sizes of approximately 10 nm.[12]

The presence of anatase in all films under investigation was also confirmed by electron diffraction (data not shown) and measured by grazing-incidence X-ray diffraction (GI-XRD). The electron diffraction experiments on AMPS-grafted substrates also revealed that the crystallites in Figure 9a and b were preferably aligned with their (001) plane parallel to the imaging plane. A preferential orientation of the film was confirmed by the enhanced intensity of the (004) reflex compared to the (200) signal as measured by GI-XRD (Figure 10). Whereas the TiO_2 film contains parallel-arranged crystallites, the globular aggregate (Figure 9b) shows radially oriented crystallites originating from a central nucleation point. Therefore it can be concluded that the columnar crystals grow in the [001] direction; TiO_2 homogeneously precipitated in the LPD solution thus follows the same growth mechanism as the films deposited on grafted polystyrene. DeGuire et al. made analogous observations for films prepared on self-assembled monolayers under similar LPD conditions.[16] These authors postulate that a preferred nucleation of polar planes of anatase on the highly charged SAMs contributes to the *c*-axis-oriented growth.

In summary we believe that the textural effects observed for TiO_2 films on polystyrene is caused by growth anisotropy of the respective crystallites. The later directional deposition and columnar growth, however, is rather caused by spatial restrictions due to adjacent nucleation sites (Figure 8) than by substrate-related factors such as oriented nucleation phenomena.[17]

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(16) Pizem, H.; Sukenik, C.; Sampathkumaran, U.; McIlwain, A.; De Guire, M. *Chem. Mater.* **2002**, *14*, 2476.

(17) Rodriguez-Navarro, A.; García-Ruiz, J. *Eur. J. Mineral.* **2000**, *12*, 609.

Table 1. Summary of Results of Film Deposition Experiments by TiO_2-LPD on Polystyrene after Different Surface Modification Procedures

		film properties				
surface treatment	contact angle[a] [°]	15 min. (AFM)	3 h (SEM)	> 3 h	XRD orientation[b]	film adhesion
none	90		(partial coverage with rough grains)[c]	closed film[c]	[c]	poor[d]
etching (H_2SO_4/SO_3)	30 → 60	no material deposition	single hemispheres w. rough surfaces	single grown hemispheres	none	no film
grafting (AMPS)	30 → 45	coverage with fine grains	fine grained film, single deposits f. solution	closed film	yes	good
hydroxylation ($Na_2S_2O_8$)	50 → 70	single fine grains	partial coverage with rough grains and single deposits f. solution	closed film	yes	good

[a] Wetting angles directly after surface modification and → after 24 h. [b] As determined by GI-XRD of films after 18 h mineralization by intensity ratio of (004) and (200) reflexes. [c] Film characterization on substrate difficult due to poor adhesion. [d] Film delaminates when treated with sharp water jet.

The results obtained for the liquid phase deposition of TiO_2 on differently functionalized polystyrene surfaces are summarized in Table 1. It is important to note that in the case of etching the increase of hydrophilicity does not necessarily lead to a high density of nucleation sites and subsequent formation of continuous TiO_2 films. In contrast, material deposition on etched polystyrene is essentially inhibited compared to the other hydrophilic surfaces prepared by grafting and hydroxylation. On the other hand, continuous films are formed even on untreated PS, but they show poor adhesion to the substrate and are easily removed by a strong water jet.

The interrelationship between nucleation, film growth, and adhesion is best understood for the AMPS grafted surface where a multitude of nucleation sites is provided quickly leading to columnar film growth. The subsequent good adherence may well be mediated by these contact points. Even though the density of nucleation sites on hydroxylated PS is significantly lower and the film is starting to cover the surface completely after 3 h, the film adhesion is also high. Although no significant differences in the material deposition on untreated polystyrene were observed, these films easily delaminate from the surfaces. AFM imaging (Figure 2) revealed that untreated samples are even slightly rougher than the modified polymer surfaces, which would rather favor better adhesion of subsequently deposited films.

On the basis of the present results it may be postulated that TiO_2 nucleation is not necessarily facilitated by an increased hydrophilicity of the polymer surface, but the adherence of a film is mediated by electrostatic interactions as pointed out by De Guire et al.[16] It must be noted, however, that the understanding of modified polymer surfaces is much more complicated than that of well-characterized SAMs due to the complexity of these systems.

4. Conclusions

Partially crystalline TiO_2 films can be successfully deposited on polystyrene. Both nucleation and film adhesion critically depend on the surface modification of the polymer. The material deposition is characterized by initial heterogeneous surface nucleation and growth from these starting points until the interconnection of sites eventually leads to the formation of continuous films. Because of the observed preferential growth of TiO_2 along the *c*-axis of anatase, the subsequent film growth proceeds in a columnar fashion.

High polymer hydrophilicity is not a necessary criterion for film formation, but satisfactory adhesion was found only on surfaces which showed a good wetting behavior. Best results were obtained for surfaces wet chemically grafted with AMPS or treated with an aqueous $Na_2S_2O_8$ solution. This simple wet chemical hydroxylation procedure does not require vacuum-based plasma activation as the grafting reaction and therefore is advantageous in the sense of biologically inspired materials synthesis.

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