Stamping of Monomeric SAMs as a Route to Structured Crystallization Templates: Patterned Titania Films

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Abstract: Gold-coated glass slides have be patterned by using self-assembled monolayers (SAM) of alkane thiols. Through the use of a special thiol terminated with a styrene monomer, microstructures of 5 to 10 μm width and 70 Å height have been formed on the surface by graft polymerization of styrene. These patterned gold slides have then been used to template the precipitation of thin titania films from ethanolic solutions of titanium isopropoxide to create microstructured architectures in the film. Plasmon resonance spectra have established the presence of different steps in the process and have been used to follow the kinetics of the precipitation of titania on the surface. The structured TiO_2 films have been characterized by scanning electron microscopy.

Keywords: films · scanning probe microscopy · self-assembly · surface analysis · titania

Introduction

There is currently an intensive effort to develop materials with a wide range of properties that open up new opportunities in fields such as catalysis, separation technology,[1, 2] electronics[3] or optics.[4] Many of these materials are made by using self-organizing systems, such as surfactant liquids and biological systems as templates for the deposition of inorganic materials in the form of thin films. Titanium dioxide has been of special interest because of its relatively high refractive index ($n = 2{,}88$ at $\lambda = 620$ nm). Another challenge is to produce patterned materials, for example as photonic materials. Several methods have been employed towards this end. Surfactants have been used to pattern micropores in titania,[5] microlithography[6] and colloidal suspensions[7] that spontaneously form colloidal crystals were employed for the template growth of porous material. In this contribution, we suggest the possibility to structure titania thin films by micropatterning, a powerful method which has been used most widely for preparing organic films (self-assembled monolayers, SAMs) with specific surface properties. Microstructures can be obtained by soft lithographic patterning, usually involving combinations of chemical etching, stamping, and photolithography.[8] In previous studies we employed SAMs of various thiols for a number of applications such as direct crystallization or polymerization catalysis.[9] The use of thiol monolayer surfaces on gold has been extended by us to the use of thiol coated gold colloids. This has opened new dimensions in the chemistry of protected surfaces as colloids show a similar behavior as molecules, that is they can be precipitated or redissolved. On the other hand, they still display many properties of extended surfaces. Water soluble colloids have been prepared through the use of thiols that serve as an in situ agent for protection and capping.[10] The crystallization of biominerals such as calcium carbonate[11] and iron hydroxides[12] on gold surfaces modified with different thiols has been extended to the use of protected colloids as crystallization nuclei.[13] Sticky colloids that can be used in the construction of complex composites have been prepared by means of protecting groups.[14] Whitesides and co-workers used micropatterning techniques to crystallize calcium carbonate in structured regions on self-assembled monolayers. The crystallization can be made very sensitive to the structure and the patterned surface induces the nucleation itself.[15] Knoll and co-workers have established the chemical deposition of thin lead sulfide films. The self-assembled monolayers control the deposition rate of PbS, the size, and the orientation of the PbS thin film.[16]

In the present work, we introduce a new styrene monomer **1** which combines a monomeric moiety that can be polymerized, with a functionality that permits cleavage of the polymer from the surface through breaking an ether bond. Our thiol

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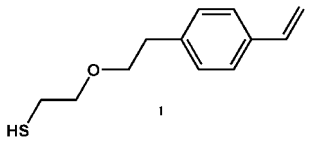
  0947-6539/00/0622-4149 $ 17.50+.50/0

has been inspired by reports by Ulman and co-workers on the possibility of anionic polymerization of styrene-derived thiols on gold surfaces.[17] The resulting layers are invested with high stability and high grafting density, and are preferred in nano-applications which require structurally rigid and compact behavior of the monolayer. Polymers such as polystyrene and polyethyloxazoline can be photochemically attached to surfaces over fixed benzophenone derivatives.[18] Zhao and Brittain have established the synthesis of block-polymers on surfaces by carbocationic and atom transfer radical polymerization.[19] Well defined polymer–nanoparticles can be obtained by living radical polymerization on SiO_2 nanoparticles.[20]



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Self-assembled monolayers can be made on gold(111) surfaces by exposing glass slides evaporated with a fresh gold film to alkane thiol solutions. Thiol monolayers are fixed chemically to gold surfaces with a strong gold–thiol bond.[21] The monomer **1** was modified to carry a free mercapto group for linking it to gold surfaces. Because the gold-thiol linkage is not easily cleavable, a breakage was introduced through an ether bond. This special structural feature opens various possibilities for modifying surfaces in general. Thiols with more than one functionality in one molecule promise many ways to new nano-material technologies.

By using the stamping technique[22] the mercapto–styrene monomer could be patterned on the gold surface. This very hydrophobic monomer is not soluble in solvents such as alcohols and water. By using hydrophilic stamps, we patterned gold surfaces with a nonfunctionalized alkane thiol, which is soluble in ethanol and spreadable on the stamp surface. Then the functionalized mercapto styrene monomer was spontaneously assembled from toluene solution.[23] After anionic polymerization with unfunctionalized styrene, structures of polystyrene appear on the surface which correspond to the original stamp structure. These structures can not be removed from the surface both by simple washing or even by harsher methods such as soxhlet extraction with boiling toluene.

The assembly of the thiol monomer (on normal gold surfaces) can be followed by plasmon resonance spectroscopy, as can the polymerization, and the cleavage of the polymer from the surface through breaking the ether linkage. Kinetic experiments monitoring the precipitation of titania were also made using plasmon resonance spectroscopy, by following the thickness of titania as a function of time. But this technique demonstrated in this work can be used in tailoring crystal structures by using selected monomeric SAMs.

Results and Discussion

Figure 1 shows the schematic procedure to produce structured thin titania films. Starting with monomer/alkane thiol structured gold slides, the polymerization leads to a pre-structured

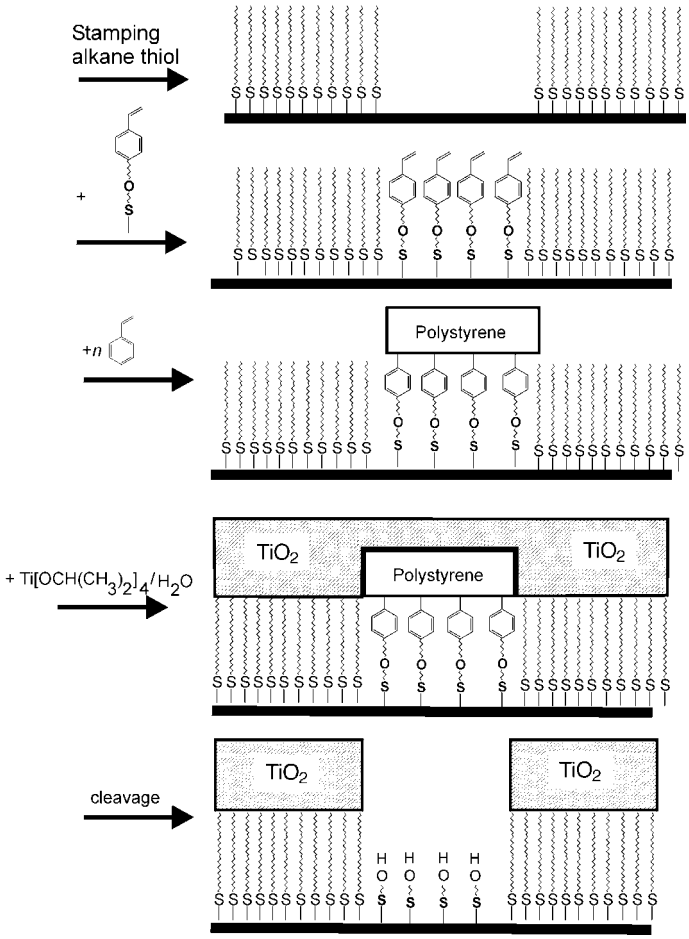

Figure 1. Schematic illustration of the formation of thin, structured titania films. The gold surface is patterned with an alkane thiol and then with the monomer **1**. After polymerization, blobs of polystyrene are obtained in the area of the patterned monomer. The other areas are not affected by the manipulation. Titania is then precipitated all over the surface. After the cleavage of the polymer, the titania over the polymer blobs is removed.

surface. Titania can be precipitated by diffusing water into an ethanolic titanium isopropoxide solution. The inorganic material covers the entire surface. The film formed in this fashion is physically stable and strong enough to withstand the following chemical modifications on the surface.

Cleavage of polystyrene on gold surfaces: The plasmon resonance spectrum was collected against ethanol on bare gold slides, after coating with the thiol monolayer **1**, after polymerization of the assembled monomer **1**, and after cleavage of the polymer from the surface. Figure 2 displays the corresponding SP spectra of the experiments b) and a closer view of the corresponding minima a). The shifts of the plasmon curves corresponding to angular changes of 0.6° (monomer–bare gold), 0.9° (polymer–bare gold) and 0.43° (removed polymer–bare gold) and could be fitted using the Fresnel formula. Assuming that the refraction indices of thiol **1** and of the polystyrene layer are not different from that of bulk styrene ($n = 1.5470$) and bulk polystyrene ($n = 1.5760$), the thicknesses of both SAMs on gold were determined to 16 Å in case of the monomer and 70 Å in case of the polymer.

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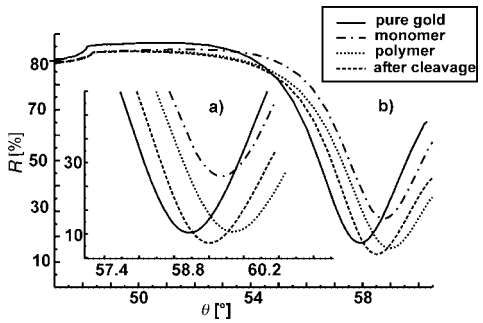

Figure 2. Surface plasmon resonance spectra of the bare gold-coated surface (——) after self-assembly of the monomer (– – –), after polymerization (···) and after cleavage of the polymer (•–•–). a) Detailed view of the corresponding minima of the complete spectrum b).

After removing the polymer layer from the surface a thickness of the resulting SAM of 9 Å was determined, while assuming that their refraction index is not significantly different from those of a hydroxyalkane thiol SAM ($n = 1.5360$) on the surface. Modelling the structures of the monomer and a hydroxyethane thiol using molecular mechanics at the MM2 level (as implemented in Chem 3D, version 3.5) of the thiol **1** suggests that the chain expansions of as much as 14.3 Å are reasonable from an energetics point of view. In case of the hydroxyethane thiol a chain expansion of 5.6 Å is expected. We assume that the polymer is not quantitatively removed from the surface. Considering additional gold–sulphur bonding for the adsorbed thiols, we conclude that nearly complete monolayer coverage of the gold surface has been achieved.

Precipitation of titania on surfaces: The kinetics of the precipitation of titania on the self-assembled monolayer surfaces could be followed by using plasmon spectroscopy. Figure 3 displays the deposition through hydrolysis of titania

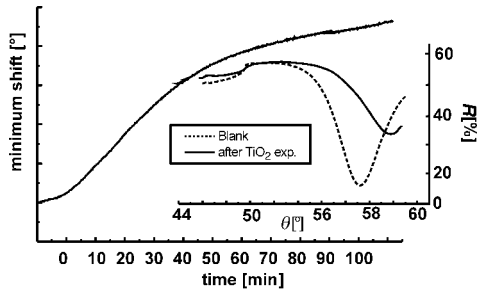

Figure 3. Plasmon resonance kinetic experiment of precipitation of titania from ethanolic solution on polymer surface. The final shift in the plasmon minimum corresponds to a film thickness of 14 Å after 140 min.

on the polymer surface from ethanolic solution of titanium isopropoxide. Here the changes in the plasmon reflectivity have been pursued using a minimum search routine monitoring the experiment as a function of time. The initial time for this experiment was taken as the time of exposure of the monolayer surface to the titanium isopropoxide solution (10 mmol) to a moist atmosphere. It can be seen that the near-saturation in the reflectivity takes as long as 120 min. Plasmon spectroscopy experiments showed shifts of the plasmon curves after 200 min reaction time, which corresponds to a film thickness of 14 Å assuming a refractive index which is not much different to that of titania ($n = 2.8300$).

The experiment shows that the reaction time has a influence on the film thickness only in the beginning. After saturation standardized films of titania can be obtained which can be deduced from insignificant changes of the film thickness after 2 h.

Scanning electron microscopy: Titania can be precipitated from a 10 mmol solution of titanium isopropoxide in ethanol under conditions described in the Experimental Section. Figure 4 displays a scanning electron micrograph of spheres of

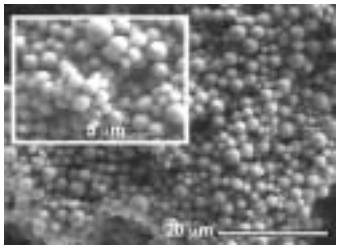

Figure 4. Scanning electron micrographs of the precipitation of titania from ethanolic solution in absence of a self-assembled monolayer surface.

titania thus obtained. The size of these filled particles ranges from 1 to 2.5 µm. They aggregate on the bottom of the reaction vessel as a porous material.

Gold surfaces were patterned with hexadecane thiol and were then placed in a 10 mmol toluene solution of the prepared monomer **1**. These patterned areas can be polymerized in toluene with butyl lithium and additional styrene monomer. The SE micrograph in Figure 5 displays the

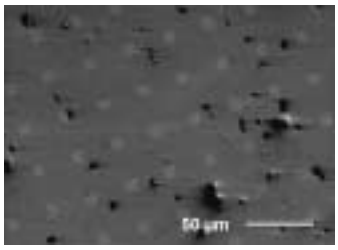

Figure 5. Scanning electron micrograph of a patterned gold surface after polymerization. The light dots correspond to the polymer, the dark area to the stamped alkane thiol structure.

resulting surface after the polymerization. The obtained regular polymer dots have a size of 10 µm which corresponds to the size of the stamp pattern. The surfaces thus prepared can be used to precipitate titania under the same conditions as discussed above. Figure 6 displays a SE micrograph of titania obtained on the templated surface. At this stage, titania aggregates on the surface in the form of a continuous thin film, and the surface is fully covered. After 24 h the gold slides were washed with fresh ethanol and transferred into a reaction vessel which contained a solution of trimethyl silyl chloride in dichloromethane to split the polymer layer with titania above from the gold slide surface.

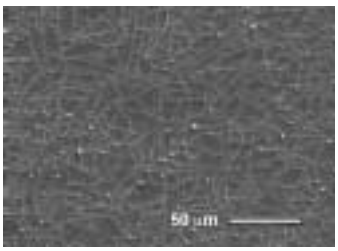

Figure 6. Scanning electron micrograph of a patterned and polymerized gold surface after precipitation of titania from ethanolic solution of titanium isopropoxide.

A surface which results normally after the cleavage procedure is displayed in Figure 7. The dark hollows correspond to the patterned polymer surface. The patterned

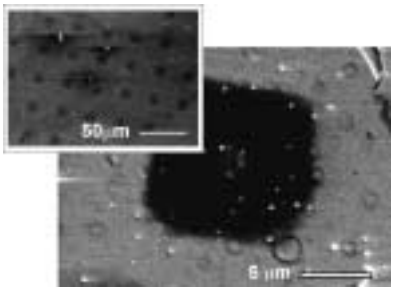

Figure 7. Scanning electron micrograph after cleavage of the ether bond in the previous surface. Regular hollows are obtained in the thin titania film.

structure is seen to be quite sharp with the edge resolution being better than 1 μ. From the SE micrographs, we venture to say that the patterns in the titania films are nearly as well defined as the patterns in the original stamp. EDX measurements, which can be made simultaneously during the scanning electron microscopy experiment, verify the absence of titania in the hollows and presence in the area around (Figure 8). As

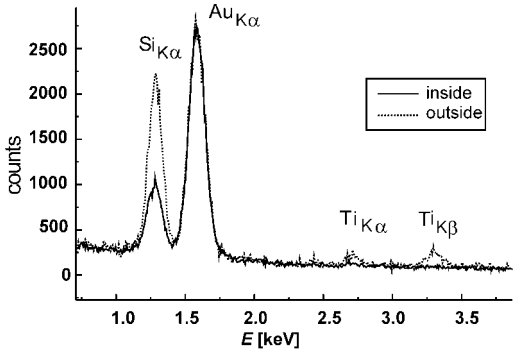

Figure 8. Energy dispersive X-ray measurement from the area inside the hollows (dots) and from the outside area (solid). Titanium K_α and K_β peaks cannot be found inside the hollows after removing of the polymer/titania surface (see Figure 7).

the electrostatic charging of the insulating titania leads to dark spots in the SEM image the area around the hollows can be assigned to the titania covered surface. Using simple SAM surfaces (without forming polymers on them) surface titania could not be removed through cleavage of the ether bond breaking.

Conclusion

In this paper we have presented a new way to pattern thin films of inorganic oxides using templates of self-assembled polymeric monolayers. Their architectures are obtained through combination of organic synthesis and stamping techniques. Organic thiols posses a high stability on such gold surfaces and lend themselves well for further manipulations to yield surfaces with new characteristics. We show that it is possible to polymerize prestructured areas filled with monomeric thiol molecules. These patterned surfaces can be used as templates for crystallization, and in this work, we present titania as an example. Experiments are currently under way to use these surfaces to crystallize other compounds utilizing the different behavior of the functionalized thiols and polymers. This work also shows that it is possible to perform a wide range of modifications of surface-bound organic compounds after crystallization has taken place. The thin inorganic films have the specific structure of the stamp. It is obvious that these patterned films have a number of potential applications, the only limitation being the number of structures that can be made with stamping techniques.

Experimental Section

All experiments were carried out an inert gas atmosphere. Solvents were purchased from Riedel de Haën Chemicals and used without further purification. Toluene was dried over sodium before use in polymerization. Styrene (Aldrich Chemicals) was freshly distilled to remove the stabilization agent.

Instrumental techniques: SPS measurements were performed in the Kretschmann configuration[24] against ethanol. Optical coupling was achieved with a LASFN 9 prism ($n = 1.85$ at $\lambda = 632.8$ nm) and index matching fluid ($n = 1.70$) between prism and the BK270 glass slides. The plasmon was excited with *p*-polarized radiation using a He/Ne laser (632.8 nm, 5 mW). The glass slides (3.5×2.5 cm) were cleaned with aq. NH_3/H_2O_2/water 1:1:5 10 min at 80 °C and coated with gold using a Balzers BAE250 vacuum coating unit under pressure of less than 5×10^{-6} hPa, typically depositing 48 nm of gold after first depositing 3 nm of Cr. The slides were exposed to the organic thiol solution (10 mmol) for 24 h.

Scanning electron microscopy was performed with a ZEISS digital scanning microscope 962 combined with a Kevex EDAX at acceleration potentials of 5–15 kV. The glass substrates were cut in small pieces and fixed with conducting glue on alumina sample holders and used without further coating.

Preparation of the thiol 1: The monomer **1** was achieved by using modified procedures of Braun and Keppler,[25] Sieber and Ulbricht.[26] The thiol group was obtained using the Bunte salt method.[27–29]

(2-Hydroxy-ethyl)-phenylethyl-ether (a): A mixture of sodium (8 g) and phenyl ethanol (100 g) were heated up to 70 °C. After the sodium was fully dissolved the reaction mixture became solid. Then bromo-ethanol (2.5 g) was slowly added and stirred at 100 °C. After 1 h the mixture was heated up to 130 °C and was stirred for further 2.5 h. After the reaction mixture was cooled to room temperature the precipitated salt was filtered off and the oily filtrate was distilled under reduced pressure (3×10^{-2} mbar). After repeated distillations the product was obtained (50%). B.p. 110–120 °C (3×10^{-2} bar); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.82$ (t, $^3J(H,H) = 6.7$ Hz, 2H; $ArCH_2$), 3.47(t, $^3J(H,H) = 6.7$ Hz, 2H; OCH_2), 3.78 (t, $^3J(H,H) = 6.7$ Hz, 4H; CH_2O-, CH_2OH), 7.19(m, 5H; ArH); MS (EI-MS): m/z (%): 166.1 (10) $[M]^+$.

(2-Bromo-ethyl)-phenylethyl-ether (b): The above product **a** (8 g) was added to a solution of HBr (40 mL) and glacial acetic acid (40 mL). The mixture was stirred under reflux for 12 h. After cooling to RT the mixture was neutralized with saturated Na_2CO_3 solution. The organic product was

0947-6539/00/0622-4152 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 22

extracted from the aqueous solution with $CHCl_3$. The organic layer was dried with sodium sulfate and the solvent was evaporated. The resulting product was used without further purification (77%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.82$ (t, $^3J(H,H) = 7.6$ Hz, 2H; $ArCH_2$), 3.53 (t, $^3J(H,H) = 7.6$ Hz, 2H; $BrCH_2$), 3.70 (m, $^3J(H,H) = 7.6$ Hz, 4H; CH_2OCH_2), 7.17 (m, 5H; ArH); IR (KBr): $\tilde{\nu} = 3087-3007$ (ArH), 2960 (CH_2, CH_3), 1120 cm^{-1} (C-O-C).

(2-Bromo-ethyl)-acetophenethyl-ether (c): $AlCl_3$ (2.2 g) was suspended in CS_2 (8 mL) and acetyl chloride (1 mL) was added. A solution of compound **b** (4 g) and acetyl chloride (4 mL) was dropped slowly to the mixture in such a way that the reaction temperature was kept at 0 °C. After stirring for 3 h at 0 °C the mixture was poured into a solution of ice and 37% HCl 4:1. The organic layer was separated, and the aqueous layer was washed with $CHCl_3$ twice. The organic phases were combined and dried with sodium sulfate, the solvent was evaporated and the residue was chromatographed from silica gel with eluent petrol ether/ethyl acetate (5:1) to yield **c** (44%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.55$ (s, 3H; CH_3), 3.1 (t, $^3J(H,H) = 6.7$ Hz, 2H; $ArCH_2$), 3.57 (t, $^3J(H,H) = 6.7$ Hz, 2H; CH_2Br), 3.87 (m, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OCH_2), 7.22 (d, $^3J(H,H) = 7.6$ Hz, 2H; ArH), 7,89 (d, $^3J(H,H) = 7.6$ Hz, 2H; ArH); MS (EI-MS): m/z (%): 272.0 (50) $[M-H]^+$.

***p*-(2-Bromo-ethyl)-styrylethyl-ether (d)**: A solution of **c** (2.5 g) in isopropyl alcohol (15 mL) was added to a mixture of aluminium isopropoxide (2.1 g) in isopropyl alcohol (15 mL). The mixture was distilled over a vigreux-column (20 cm length) at a bath temperature of 130–140 °C. The distillation was continued until acetone was absent from the distillate (control reaction with 2,4-dinitrophenyl hydrazine). Then the isopropyl alcohol was distilled off and the residual was poured into 6N H_2SO_4 (100 mL). The aqueous layer was extracted with diethyl ether three times and the combined organic layers were washed with 1N NaOH (50 mL), and subsequently three times with water (100 mL). Then $KHSO_4$ (3 g) was added to the ether solution, and the mixture was kept at room temperature. After 10 h the ether was evaporated and the residue was distilled at 200 mbar. The water was removed from the reaction mixture on a 130 °C bath. After the distillation of water ceased the bath temperature was increased to 170 °C and a colorless oil obtained at 99–105 °C in oilpump vacuum (3×10^{-2} bar) (42%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.10$ (t, $^3J(H,H) = 6.7$ Hz, 2H; $ArCH_2$), 3.50 (t, $^3J(H,H) = 6.7$ Hz, 2H; CH_2Br), 3.55 (m, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OCH_2), 5.19/5.73 (dd, $^3J(H,H) = 7.4$ Hz, 2H; $CHCH_2$), 6.66 (m, $^3J(H,H) = 7.4$ Hz, 1H; $CHCH_2$), 7.22 (m, 4H; ArH); MS (EI-MS): m/z (%): 256.2 (30) $[M-H]^+$.

***p*-(2-Mercapto-ethyl)-styrylethyl-ether (1)**: Compound **d** (0.5 g) was dissolved in ethanol (10 mL) and heated under reflux. A solution $Na_2S_2O_3$ (0.8 g) in water (10 mL) was added dropwise. The mixture was stirred under reflux for 4 h. The solvent was evaporated and 1N HCl (50 mL) was added to the residue. The mixture was heated under reflux for 2 h. The aqueous layer was extracted with CH_2Cl_2 three times, the organic phases were combined, dried with Na_2SO_4 and the solvent was evaporated. The product obtained as a yellowish oil (72%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.72$ (m, $^3J(H,H) = 6.7$ Hz, 4H; $ArCH_2$, CH_2SH), 3.88 (m, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OCH_2), 5.19/5.73 (dd, $^3J(H,H) = 7.4$ Hz, 2H; $CHCH_2$), 6.66 (m, $^3J(H,H) = 7.4$ Hz, 1H; ArCH), 7.22–7.89 (m, 4H; ArH); MS (EI-MS): m/z (%):209 (30) $[M-H]^+$.

Polymerization of structured templates: Gold slides were prepared immediately before use as described in the Experimental Section and hexadecane thiol was stamped in a patterned manner on the gold surface according to published methods.[15] The gold slides were then placed into a solution of **1** (10 mmol) in $CHCl_3$ for 10 h. The slides were washed with $CHCl_3$, dried in a N_2 stream and transferred into dry toluene. Two glass slides were placed in a reaction vessel and *n*-butyl lithium (0.5 mL) and styrene (0.2 mL) were added. The reaction mixture was stirred for 30 min at room temperature. Then styrene (1.5 mL) was added to give a dark-orange solution and the mixture was stirred for 1 h. The polymerization was stopped by adding methanol (3 mL). The templates were cleaned with $CHCl_3$ and methanol, and dried in a N_2 stream. Surface IR measurements correspond to polystyrene films as published by Ulman and co-workers.[17]

Crystallization of titania: The templates were placed face down into a reaction flask.[30] The flask was filled with ethanol (100 mL), and titanium isopropoxide (3 mL) was added. The flask was transferred into a desiccator and stored at room temperature. The precipitation was initiated by placing a Petri dish with water at the bottom of the desiccator. The diffusion experiment was stopped after 10 h, the samples were removed, washed with ethanol and dried in air.

Cleavage of the ether bond: A solution of dry $CHCl_3$ (100 mL) and trimethylsilyl chloride (100 μL) was placed in a reaction vessel fitted with a gas inlet and outlet. N_2 was passed through the mixture for 15 min. Then the titania coated templates were placed and the mixture was stirred for 1 h under N_2 atmosphere. After this time the samples were removed, cleaned with toluene and dried on air.

Acknowledgement

We thank Degussa AG, Hanau for a generous gift of chemicals. We are indepted to the Materials Science Center of the Universität Mainz and the Deutsche Forschungsgemeinschaft for partial support.

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Received: April 12, 2000 [F2418]