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Substrate-Independent Stable and Adherent Reactive Surface Coatings and their Conversion with Amines

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Summary: To create stable, adherent and reactive surface coatings, a hybrid polymer composed of poly(methylsilsesquioxane) (PMSSQ) and poly(pentafluorophenyl acrylate) PFPA with a M_n of 32000 g/mol was prepared by a RAFT polymerization procedure. These hybrid polymer has been used for coating experiments. The PFPA part enabled a variable functionalization of the coating afterwards. The stability on various substrates (e.g. glass, PMMA, steel) was tested in an ISO tape test. These reactive surface coatings were modified using different amines, such as amino-terminated PEG, dodecyl amine and *N*-isopropyl amine. The conversion was analyzed by FT-IR and contact angle measurements.

Keywords: active esters; adhesion; atomic force microscopy (AFM); films; graft copolymers; inorganic-organic hybrid polymers; PNIPAM; RAFT polymerisation; surfaces

Introduction

In various applications for research or industry hydrophilic, hydrophobic or stimuli-responsive surface coatings are of special interest.[1–8] Reactive coatings could be a precursor for simple tunable surface properties. Just using a simple modification step should convert the surface towards the desired properties or structures.

Active ester polymers are ideal candidates which can be converted by a simple polymer analogues reaction into the desired functional polymer. Just by the reaction with nucleophiles, such as amines, many functionalized polymers can be synthesized as shown in reference[9] and references therein. Attached onto a substrate the conversion could be induced by dipping it in an amine solution or by micro contact printing of amines onto the surface.

Typical methods to prepare polymeric films on a surface are grafting from polymerization or the chemical vapor deposition polymerization. Both methods were already used to prepare reactive coatings consisting of active ester monomers. Jerome et al. reported the electrografting of *N*-succinimidyl acrylate, a well known reactive ester monomer, from glassy carbon.[10–11] Lahann et al. demonstrated the chemical vapor deposition polymerization of [2.2] paracyclophane pentafluorphenol ester on silicon wafers and its conversion with amines to obtain structuralized surfaces.[12–13] Both methods yielded in reactive surface coatings but the procedures are hardly convertible to any scientific or industrial application.

Within the present study, we analyzed a reactive inorganic/organic hybrid polymer as a versatile coating material.

Experimental Part

Materials

All reagents, solvents, and substances used were of reagent grade quality and were obtained from commercial sources.

Instrumentations

The synthesized compounds were characterized by NMR-spectroscopy, mass spectroscopy, FT-IR spectroscopy and elemental

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analysis. Molecular weights of the polymers were determined by gel permeation chromatography using a PSS standard column, UV-, refractive index- and light scattering-detector. NMR-spectra were recorded on a 300 MHz Bruker FT-NMR-spectrometer using $CDCl_3$ as a solvent. Chemical shifts (δ) are given in ppm relative to TMS. IR spectra were recorded on a Nicolet 5 DXC FT-IR-spectrometer. FD mass spectra were measured using a Finnigan MAT 95 mass spectrometer. Elemental analyses were done with an Elementar Vario Micro Cube (detecting C, H, N, S). Film thicknesses were measured on an EL X-02C ellipsometer. Thermo gravimetrical analysis was performed using a Perkin Elmer Pyris 6 TGA. Atomic force microscopy (AFM) measurements were observed on a Veeco Dimension 3100.

Dithio benzoic acid 4-ethyltrimethoxysilylester (RAFT-Si)

31.6 mmol phenyl magnesium bromide was placed with 50 mL THF in a round bottomed flask. After heating to 40 °C 49.7 mmol CS_2 was added. After 15 minutes 31.7 mmol p-(chloromethyl)-phenylethyltrimethoxysilane was injected and the reaction mixture was stirred at 50 °C for 1 h. The mixture was dissolved in diethyl ether and washed with water, the ether phase was dried over magnesium sulfate, filtered and the ether was removed. The product was dried in vacuum. Yield: 25.3 mmol (79.7%). ^{1}H-NMR ($CDCl_3$) δ: 8.01 (m, 1H); 7.27 (m, 8H); 4.58 (d, 3J = 2.4 Hz, 2H); 3.59 (s, 9H); 2.76 (m, 2H); 1.04 (m, 2H). EA (%): C = 56.20; H = 6.32; S = 10.51. FD mass spectra: 391.9 (100%); 392.9 (26.9%); 393.9 (15.4%).

PMSSQ RAFT Macro Initiator

50 mmol methyltrimethoxysilane (MTMS), 2.5 mmol RAFT-Si, 20 mL THF, 500 mmol water and 10 mmol HCl were stirred at 0 °C for 3 h. The reaction mixture was dissolved in diethyl ether, washed with water. After drying, the ether was removed and the product was dried in high vacuum. ^{1}H-NMR ($CDCl_3$) δ: 7.99 (br,5H); 7.36 (br, 2H); 5.80 (br, 1.9H); 4.55 (br, 2H); 3.48 (br, 1.1H); 2.71 (br, 2H); 0.99 (br, 2H); 0.17 (br, 69.1H). M_n = 4990 g/mol, PDI = 1.63.

PMSSQ-*b*-PFPA

0.5 g PMSSQ RAFT macro initiator, 10 mg AIBN, 4 mL dioxane and 2 g pentafluorophenyl acrylate ester were placed in a Schlenk flask. The reaction mixture was stirred at 80 °C for 4 h and afterwards precipitated into *n*-hexane twice. (Yield: 1.1 g). ^{1}H-NMR ($CDCl_3$) δ: 7.40–6.85 (br); 3.05 (br, 1H); 2.81 (br); 2.32–2.10 (br, 2H)); 1.50–1.20 (br); 0.15 (br, 1H)). M_n = 32000 g/mol, PDI = 1.7.

Amino-Terminated Poly(ethyleneglycol) (H_2N-PEG500)

Amino-terminated PEG was synthesized as described in.[14]

ESI mass spectra: 550 g/mol

Surface Coating and Modification

The polymer solution was spin-coated onto clean substrates (15 s, 4000 rpm). To crosslink the inorganic block, the samples were annealed at 130 °C for 2 h and afterwards washed with THF for 30 minutes to remove any non-bonded material.

To functionalize the surface afterwards in a polymer analogous reaction the samples were placed in a 10 wt% solution of the desired amine in THF at room temperature for 1 h. To remove the excess of the amine the surface was washed several times with THF. The surface reaction was detected by FT-IR measurements using an ATR setup.

Results and Discussion

A new concept to prepare reactive surface coatings should imply reactivity, stability and adhesion on various substrates and easy application and processability.

To combine all these challenges in one material inorganic/organic hybrid polymers seems to be a promising approach. The hybridization of inorganic and organic materials on a nanometer scale offers the chance not even to combine their advantages in one material but also to achieve new, unique properties.[15]

As inorganic component poly(methylsilsesquioxane)s (PMSSQ) are known to be able to crosslink thermally and stabilize films but also as adhesion promoters on metal or metal oxide surfaces.[16] Beside these important characteristics soluble silsesquioxanes can be easily synthesized in a sol-gel process.[17] Their reactivity towards a secondary condensation in the film can be monitored using thermo gravimetrical analysis.

Connecting these fundamental properties with the reactivity of reactive ester polymers would result in a reactive coating material with high stability and easy processability.

As reactive ester monomer pentafluorophenyl acrylate emerges as a perfect candidate to build up reactive polymers, which can be converted in a polymer analogues reaction to yield a wide spectrum of functionalized polymers. One example is the conversion of poly(pentafluorophenyl acrylate) (PFPA) with isopropyl amine to yield poly(*N*-isopropyl acrylamide) (PNIPAM),[18–20] known for its stimuli-responsive behavior in water.

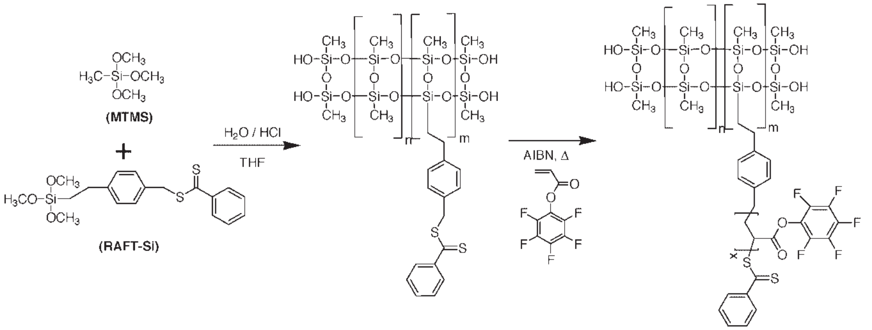
First, an inorganic/organic hybrid polymer, consisting of PMSSQ and PFPA, was synthesized as shown in Scheme 1. In the first step a PMSSQ based macro chain transfer agent is co-condensated using MTMS and the functionalized RAFT agent RAFT-Si. From this controlling agent pentafluorophenyl acrylate is grafted using usual RAFT conditions.

The obtained polymer had a molecular weight of 32000 g/mol and was soluble in THF. The thermo gravimetrical analysis of the polymer hybrid is shown in Figure 1. A secondary condensation occurs between 120 °C and 160 °C. At 400 °C the decomposition of the PFPA block could be observed.

The block ratio between the organic and inorganic block could be calculated from the mass deficits, resulting in the weight ratio of 82% PFPA and 18% PMSSQ.

The obtained hybrid polymer was spin-coated from a 10 wt% solution in THF onto silicon, glass, PMMA and steel. Afterwards the films were cured at 130 °C for 2 h to stabilize the coating by thermally induced secondary condensation as it was observed in the TGA.

The film thickness determined by ellipsometry on silicon wafer was 395 nm before curing, 375 nm after curing. The surface roughness of the films before and after curing was determined by AFM measurement, the height image after curing is shown in Figure 2, the corresponding phase images gave no additional information and were not shown in this context. The RMS value before curing is 0.471 nm, after curing 0.305 nm (both are image RMS values, calculated over 1 μm^2). Thus, the prepared surface coating on silicon is very smooth after curing.



Scheme 1.
Synthetic pathway towards reactive PMSSQ-PFPA hybrid polymers.

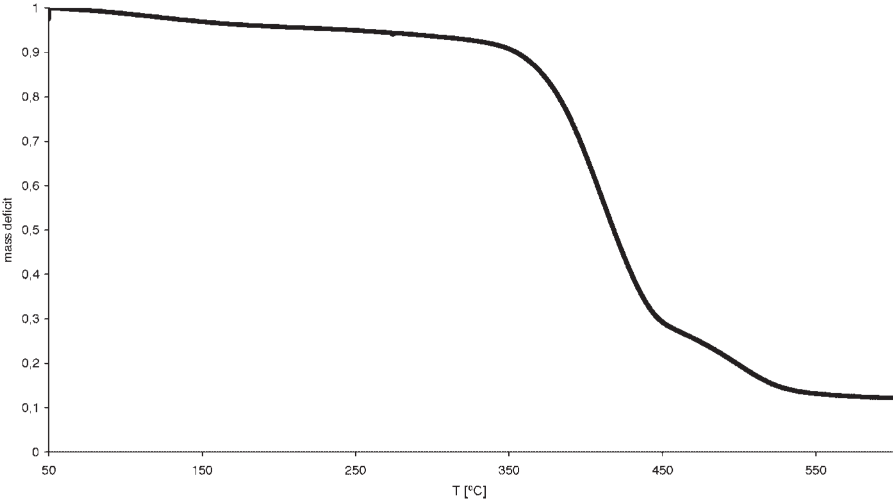


Figure 1.
Thermo gravimetrical analysis of PMSSQ-*b*-PFPA.

The adhesion and stability of the film was tested using a standard ISO tape test.[21] The test mainly focuses on the adhesion of the coating. One half of the surface coating is taped with commercially available tape. After tearing off the tape the condition of the taped and not taped surfaces are compared under microscope.

The Microscopy images of the PMSSQ-*b*-PFPA coatings on glass, PMMA and steel were analyzed. The estimated border between the taped and the not tabbed part of the surface coating is indicated by a dashed line.

The differences before and after curing are apparently on all three substrates.

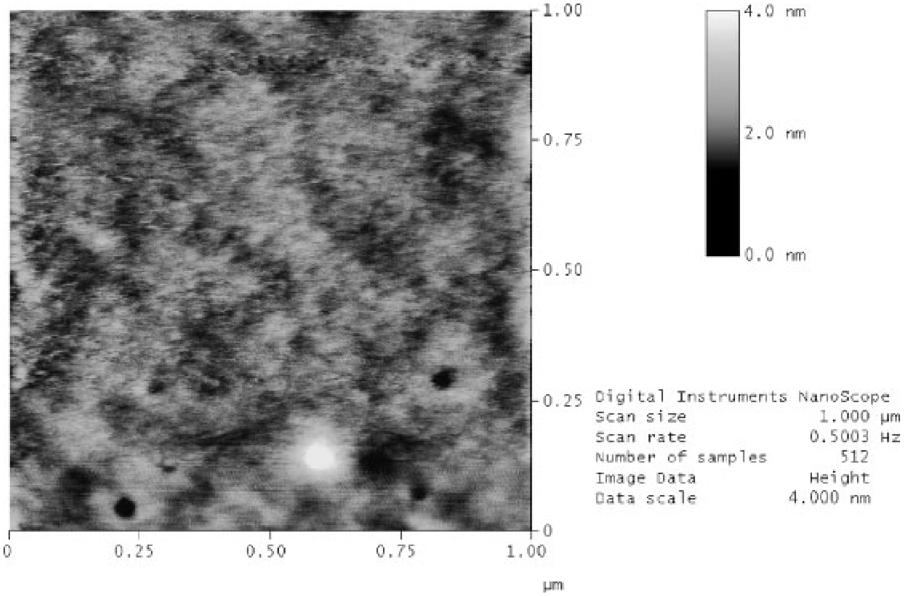
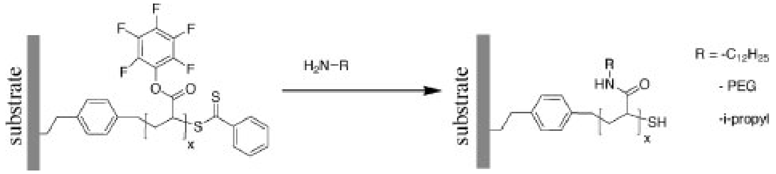


Figure 2.
AFM height image of PMSSQ-*b*-PFPA coated on silicon after curing.



Scheme 2.
Surface modification of a reactive surface by a polymer analogous reaction with different amines.

Before curing, the reactive surface coating can easily rupture off the surface. After curing, the secondary condensation results in a stable and adherent film not only on glass or steel but also on polymeric substrates like PMMA (ISO classification 4 before curing, indicating a poor adhesion on the substrate; ISO classification 0 after curing, indicating a completely maintained coating).

After proofing the ability to produce stable coatings the reactivity of the functionalized substrates were investigated. The functionalization of the surface via a polymer analogues reaction is shown in Scheme 2.

The reactive character of the obtained surfaces after spin-coating opens the possibility for a flexible functionalization procedure. As example, three case studies were conducted comprising the conversion into a hydrophilic, a hydrophobic and a temperature-responsive surface.

For the preparation of a hydrophilic surface amino-terminated PEG was used as a nucleophile in the polymer analogous reaction with the exposed active ester. Dodecyl amine was employed to create a hydrophobic surface coating, while isopropyl amine converted the reactive coating into a poly(*N*-isopropyl acryl amide) (PNIPAM) coating, which should show a temperature-sensitive behavior.

In case of *N*-isopropyl amine the conversion of the reactive coating on glass, monitored using FT-IR spectroscopy, is shown in Figure 3. The surface properties

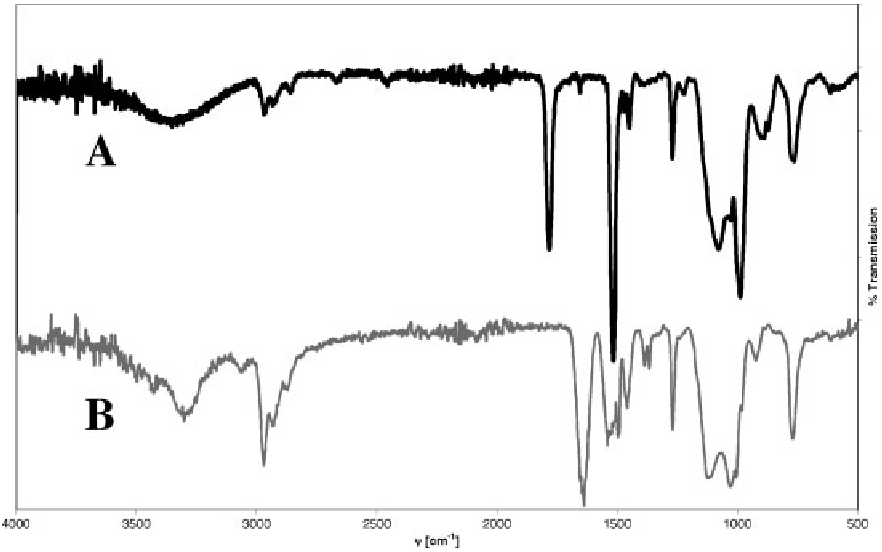


Figure 3.
FT-IR spectra proving the conversion of PFPA surface to PNIPAM surface, A: PMSSQ -PFPA coated glass after curing; B: after modification with isopropyl amine.

Table 1.
Contact angles measured on silicon, glass, PMMA and steel substrates. (If not mentioned T = 25 °C).

	silicon		glass		PMMA		steel	
	Θ_a	Θ_r	Θ_a	Θ_r	Θ_a	Θ_r	Θ_a	Θ_r
reactive surface after curing	93.3°	64.3°	94.2°	70.1°	93.0°	72.1°	92.1°	69.1°
after amino-PEG treatment	33.2°	14.9°	32.6°	12.6°	30.1°	17.9°	36.6°	16.9°
after dodecyl amine treatment	101.9°	60.1°	102.1°	60.6°	100.2°	71.1°	94.1°	63.2°
after isopropyl amine treatment	79.2°	45.0°	80.1°	52.2°	77.3°	49.0°	71.1°	49.7°
after isopropyl amine treatment (50 °C)	100.0°	68.0°	102.9°	70.2°	96.7°	72.5°	104.3°	70.2°

after conversion with amino-PEG, dodecyl amine and *N*-isopropyl amine on all substrates were investigated by means of contact angle measurements.

Spectrum A in Figure 3 shows the FT-IR of the reactive coating, which is characterized by the band at 1772 cm^{-1}, a unique signal for the activated ester bond. After the polymer analogous reaction with isopropyl amine the characteristic band at 1772 cm^{-1} disappeared completely (see Figure 3B) and the characteristic bands for an amide at 1638 cm^{-1} and 1530 cm^{-1} were found, proving a complete conversion of all active ester groups. Additionally a band at 3300 cm^{-1}, characteristic for a NH-bond appeared. Both spectra showed the characteristic bands of the PMSSQ block between 1270 cm^{-1} and 900 cm^{-1}, respectively. FT-IR spectroscopy proved a successful surface modification also with amino-PEG and dodecyl amine.

To investigate the surface behavior of the different coatings contact angles of water were measured on functionalized glass and silicon substrates. The advancing and the receding contact angles of a drop of water on the surface using an image processing software were determined. Averaged values of six independent measurements for each film are summarized in Table 1.

In principle the conversion of the reactive coating works on all tested substrates. The resulted contact angles are almost equal and seem not to be influenced by the nature of the substrate. The reaction with amino-PEG resulted in a hydrophilic surface (Θ_a between 30° and 37°). Dodecyl amine converts the reactive coating to a hydrophobic coating ($\Theta_a > 90°$).

The conversion with *N*-isopropyl amine to a PNIPAM surface resulted in a stimuli-responsive surface behavior. At a temperature below the lower critical solution temperature (LCST) the surface shows a more hydrophilic behavior. When heated above the LCST the surface behavior turns hydrophobic. The values correspond well with the literature values of PNIPAM

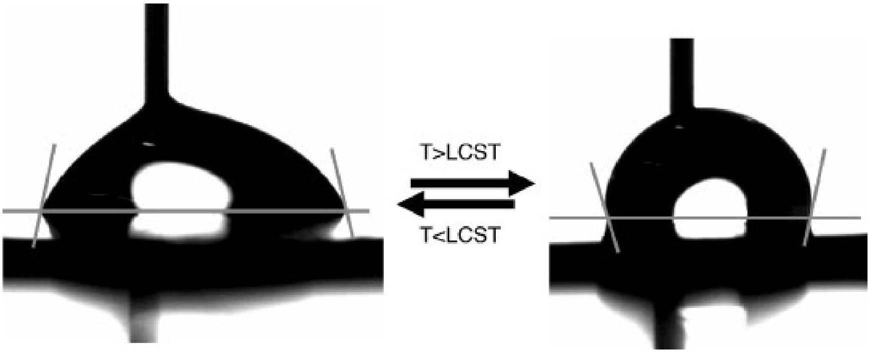


Figure 4.
Contact angle images of the stimuli-responsive coating on silicon, obtained by the conversion of the reactive coating with *N*-isopropyl amine. The left picture is taken at T = 25 °C, the right picture at T = 50 °C.

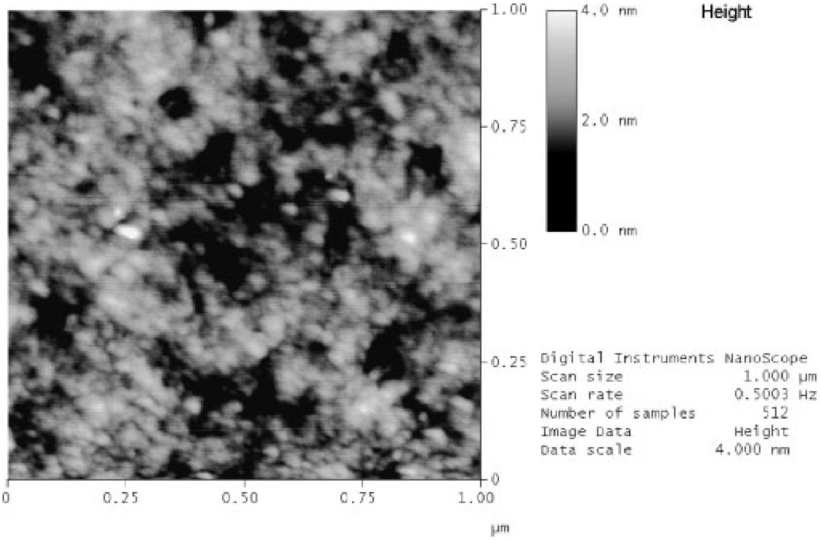


Figure 5.
AFM height image of PMSSQ-*b*-PFPA coated on silicon after curing after conversion with *N*-isopropyl amine.

functionalized surfaces, produced by other methods.[22–23]

The switching of contact angles by temperature on a silicon substrate is shown in Figure 4.

The surface roughness after conversion to a PNIPAM surface was determined using AFM (see Figure 5). The image RMS value is 0.479 nm (calculated over 1 μm^2). Compared with the reactive coating the surface roughness does not change due to the functionalization.

Conclusion

Preparing reactive surface coatings from a PMSSQ-based precursor just by spin-coating and curing seems to an easy processable and applicable method.

Obtained reactive surfaces can be converted completely just by dipping in amine solutions at room temperature. Hydrophilic, hydrophobic and also stimuli-responsive surfaces could be prepared on different kind of substrates.

The most important issue on surface coatings is the stability and adhesion on the substrate. Using the tape-test the stability of the thermally cross-linked coating could be proved on silicon, glass and steel, which can be explained by covalent bonds from the PMSSQ part to the substrate. In addition the stability of the coated film itself is high enough to obtain stable reactive coatings also on polymeric substrates.

Beside the reactivity and stability of the surface coatings prepared by PMSSQ-PFPA hybrid materials, the films are before as well as after conversion very smooth.

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