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Temperature-Responsive Surface Coatings Based on Poly(methylsilsesquioxane)-hybrid Polymers

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Summary: The present paper presents a new method to build up temperature-responsive surfaces. First a poly(silsesquioxane)-block-poly(N-isopropyl-acrylamide) (PMSSQ-*b*-PNIPAM) was successfully synthesized using RAFT polymerization. Spin-coating or dip-coating of PMSSQ-*b*-PNIPAM onto glass surfaces resulted in temperature-responsive surfaces. Surface ATR FT-IR measurements proofed the successful surface modification using PMSSQ-*b*-PNIPAM. IR fine structures of PNIPAM and PMSSQ could be assigned, respectively. In capillary rise experiments a change of the meniscus height measured at temperatures below or above LCST was observed, indicating a different wetting behavior. Thus, a simple spin- or dip-coating step results in a clean and temperature-responsive surface.

Keywords: atom transfer radical polymerization (ATRP); block copolymers; inorganic-organic hybrid polymers; lower critical solution temperature (LCST); reversible addition fragmentation chain transfer (RAFT); stimuli-responsive polymers; surfaces

Inroduction

Poly(N-isopropylacrylamide) (PNIPAM) exhibits a reversible, temperature-dependent soluble/insoluble transition at its lower critical temperature in aqueous media. The lower critical solution temperature (LCST) of PNIPAM in water was found to be around 32 °C.[1–5] It is known, that the phase transition of PNIPAM accompanies not only a drastic confirmation change from a coil to a globule, but also a rapid change in interfacial properties.[8–10] Recently, there have been many reports on grafting of PNIPAM onto solid surfaces for both scientific and engineering purposes.[6–10]

Below the LCST a PNIPAM coated surface shows a hydrophilic behavior, when heated above the LCST the behavior changes to hydrophobic.[6] This effect on substrates offers the ability to control important interfacial phenomena such as wetting,[11,12] fluid flows[13] and adhesion[14,15]. Further, the reversible adsorption of biomolecules on surfaces is of special interest.[16]

Two main routes of preparing covalent linked PNIPAM surfaces are well known. End group functionalized PNIPAM is bonded directly to an oxidized silicon surface in a polymer analogues esterfication[17] or ATRP initiators are directly linked to the surface and PNIPAM is grafted from the surface.[6] In both cases several surface preparation steps have to be performed.

Within the present study, we introduce a new surface functionalization method which allows the preparation of the coating material in solution and attach it covalently to the surface in one single coating step. In order to combine the linkage part and the temperature-sensitive part in one block copolymer, inorganic-organic hybrid polymers were used. A poly(methylsilsesquioxane) (PMSSQ) block enabled the attachment on glass surfaces, a PNIPAM block provided the temperature-responsive behavior.

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Experimental Part

Materials

All reagents, solvents, and substances used were of reagent grade quality and were obtained from commercial sources. NIPAM was recrystallized from *n*-hexane. CuBr was stirred over acetic acid, filtered off, washed with methanol and dried in vacuum.

Instrumentations

The synthesized compounds were characterized by NMR-spectroscopy, mass spectroscopy and elemental 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) were 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).

p-(Chloromethyl)-phenylethyltrichlorosilane (1)

1 was synthesized in a hydrosilylation reaction of *p*-chloromethylstyrene with Silicochloroform. 100 mg of platinum on charcoal and 100 ml toluene were placed in a round bottomed flask, 75 mmol trichlorosilane and 50 mmol *p*-chloromethylstyrene were added. The reaction mixture was stirred for 48 h at 110 °C. After filtering over celite the solvent was removed and the crude product was distilled at $2.5^{*}10^{-3}$ mbar. The yield of **1** was 39 mmol (77.1%). ^{1}H-NMR ($CDCl_3$) δ: 7.34 (d, $^3J = 8.1$ Hz, 2H); 7.22 (d, $^3J = 7.8$ Hz, 2H); 4.58 (s, 2H); 2.90 (m, 2H); 1.74 (m, 2H). EA (%): C = 38.70; H = 3.73.

p-(Chloromethyl)-phenylethyltrimethoxysilane (2)

To 100 ml methanol 35 mmol of **1** was added. After stirring over night the solvent was removed and the product was dried in vacuum (Yield: 31 mmol, 87.8%). ^{1}H-NMR ($CDCl_3$) δ: 7.29 (d, $^3J = 8.1$ Hz, 2H); 7.20 (d, 3J = 8.1 Hz, 2H); 4.55 (s, 2H); 3.56 (s, 9H); 2.73 (m, 2H), 0.99 (m, 2H). EA (%): C = 53.38, H = 7.22. FD mass spectra: 273.9 (100%); 274.9 (15.6%); 275.9 (38.9%).

Dithiobenzoic 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 **2** was injected and the reaction mixture was stirred for 1 h at 50 °C. The mixture was dissolved in ether and washed with water, the ether phase was dried over magnesium sulfate, filtered and 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 for 3 h at 0 °C. The reaction mixture was dissolved in 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*-PNIPAM

0.5 g PMSSQ RAFT macro initiator, 10 mg AIBN, 4 mL dioxane and 2 g NIPAM were placed in a Schlenk flask. The reaction mixture was stirred 4h at 80 °C and afterwards two times precipitated in *n*-hexane. (Yield: 1.9 g). ^{1}H-NMR ($CDCl_3$) δ: 7.91 (br); 7.30 (br); 6.52 (br); 4.50 (br); 3.62 (br); 2.88 (br); 2.25 (br); 1.21 (br); 1.14 (br); 0.83 (br); 0.13 (br). Mn = 23430 g/mol, PDI = 3.2.

2-Bromoisobutyric acid 5-(Trichlorosilyl)Pentyl Ester (ATRP-Si)

Synthesis analog[18]. Bp. 104 °C at 7*10^{-3} mbar. Yield: 44 mmol, 88.0%. ^{1}H-NMR (300 MHz, CDCl3): δ: 4.11 (t, ^{3}J = 6.6 Hz, 2H); 1.86 (s, 6H); 1.66 (m, 2H), 1.57 (d, ^{3}J = 6,9 Hz, 2H); 1.47 (d, 3J = 6,6 Hz, 2H);1.38 (m, 2H).

PMSSQ ATRP Macro Initiator

Synthesis analog[18]. ^{1}H-NMR ($CDCl_3$) δ: 5.55 (br); 4.14 (br, 2H); 3.44 (br); 1.91 (br, 6H); 1.77 (br, 2H); 1.42 (br, 2H); 0.63 (br, 2H); 0.13 (br, 57.2H).

Surface Coating

Standard glass plates and glass tubes were used as surfaces. The glass tubes had an inner diameter of approximately 0.6 mm an a length of 80 mm. Both were cleaned with acetone and methanol and dried with nitrogen. Solutions of PMSSQ-*b*-PNIPAM, **ATRP-Si** and ATRP macro initiator (10 wt% in THF) were prepared. These polymer solutions were either spin-coated onto the clean glass plates (15 s, 4000 rpm) or glass tubes were dip-coated into the polymer solution for 20 minutes.

Preparation of PNIPAM Coating A

A reference PNIPAM coating A was prepared using grafting-from polymerization of NIPAM from the glass surface (Figure 1). After **ATRP-Si** was coated onto the glass surface, the glass plates or tubes were washed five times with THF to remove unattached molecules. ATRP was then carried out in a degassed aqueous solution consisting of 30 mL millipore water and 2 g NIPAM. 50 mg CuBr were added and the solution was kept at room temperature for 1 hour. To remove free material the glass plates and tubes were taken out and washed several times with THF and water.

Preparation of PNIPAM Coating B

Similar to the preparation of PNIPAM coating A, the PMSSQ ATRP macro initiator was coated onto the glass surfaces. After washing with THF the samples were cured for 2 h at 130 °C. The grafting-from polymerization of NIPAM was accomplished in the procedure described above.

Preparation of PNIPAM Coating C

A 10 wt% solution of PMSSQ-*b*-PNIPAM in THF was coated onto the glass surface as described above. To fix the polymer onto the surface, the surfaces were heated in THF solution for 30 minutes to 50 °C and washed several times with THF.

Results and Discussion

It is the intention of the present study to compare different coating procedures in order to receive temperature-responsive surfaces. Temperature-responsive behavior can be achieved using poly(N-isopropylacrylamide) (PNIPAM), known for its LCST at 32 °C in water. Three different approaches have been performed to prepare PNIPAM coated surfaces: a) grafting-from atom transfer radical polymerization (ATRP) of NIPAM using a low-molecular weight initiator, b) grafting-from ATRP of NIPAM using a high-molecular weight PMSSQ based initiator, and c) coating of a

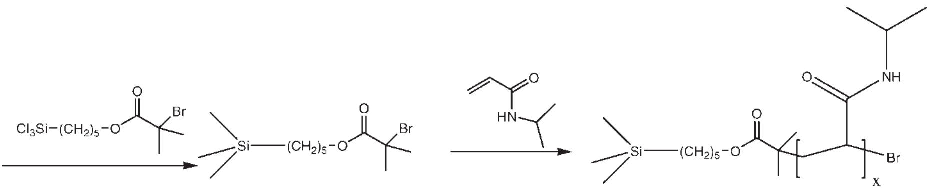
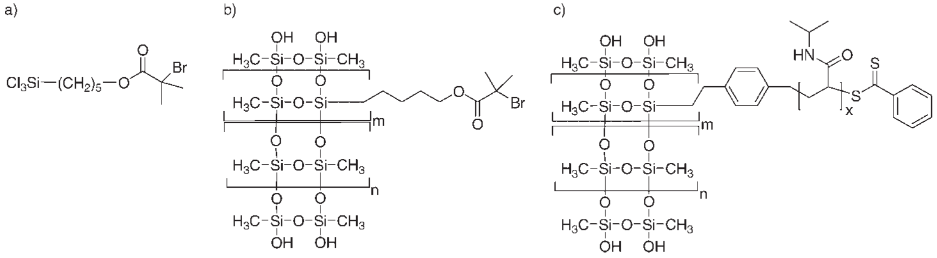


Figure 1.
Preparation of PNIPAM coating by grafting-from polymerization of NIPAM from functionalized glass surfaces.



Scheme 1.
Different coating materials: a) **ATRP-Si** initiator, b) PMSSQ ATRP initiator and c) PMSSQ-b-PNIPAM.

PMSSQ-*b*-PNIPAM polymer. The respective structures are shown in Scheme 1.

Synthesis

In the first step, three different coating materials have been synthesized. **ATRP-Si** was prepared as described previously in a two-step synthesis by esterification of 4-pentenol with 2-bromo-isobutyric acid bromide, followed by a hydrosilylation with trichlorosilane.[18]

The corresponding PMSSQ based ATRP initiator was then synthesized using **ATRP-Si** by co-condensation with MTMS under acidic catalysis.[18]

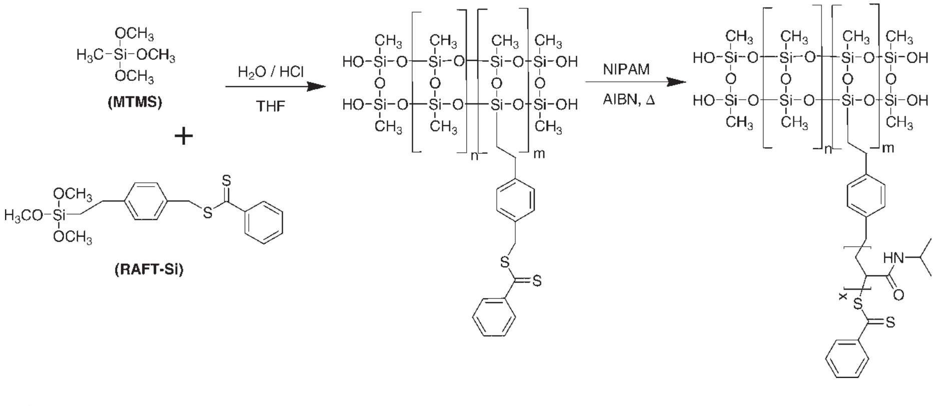
As a third route, RAFT polymerization using a PMSSQ based RAFT agent was investigated. Thus, dithiobenzoic acid 4-ethyltrimethoxysilylester (**RAFT-Si**) was prepared in a three-step synthesis. First, *p*-chloromethylstyrene was hydrosilylated with trichlorosilane using a Pt/C catalyst. The resulting trichlorosilane was then transformed into the corresponding trimethoxy compound by reaction with methanol. In the final step, the dithiobenzoic acid group was introduced by nucleophilic substitution of the chlorine yielding **RAFT-Si**.

The trimethoxysilyl RAFT agent (**RAFT-Si**) was then co-condensated with methyltrimethoxysilane (MTMS) to give a PMSSQ RAFT macro initiator, as shown in Scheme 2.

In a second step N-isopropylacrylamide (NIPAM) was grafted-from the prepared PMSSQ RAFT macro initiator using typical RAFT polymerization conditions in solution to yield a PMSSQ-PNIPAM block copolymer as shown in Scheme 2.

Surface Coating

All prepared coating compounds were then coated onto glass surfaces. A reference PNIPAM coating A was prepared using grafting-from polymerization of NIPAM



Scheme 2.
Synthesis of PMSSQ-b-PNIPAM via RAFT polymerization.

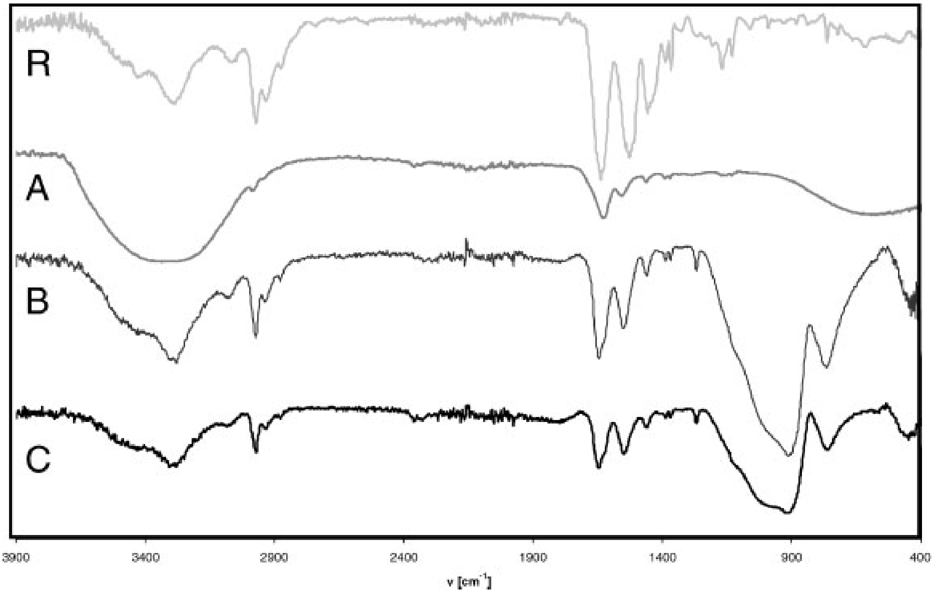


Figure 2.
R: PNIPAM reference spectra; A: PNIPAM coating (A) on glass surface; B: PNIPAM coating (B) on glass surface; C: PNIPAM coating (C) on glass surface.

from the glass surface, as shown in Figure 1. The analogue PMSSQ macro initiator for ATRP was also coated onto glass surfaces and PNIPAM was grafted-from its initiating species under ATRP conditions in water resulting in a thin PNIPAM film on the surface.

At last, the PMSSQ-*b*-PNIPAM hybrid polymer was coated onto glass surfaces from a THF solution via spin- or dip-coating and fixed by slight temperature curing (50 °C, 20 min).

All described methods resulted in PNIPAM coated surfaces.

The three different PNIPAM surfaces were characterized via ATR FT-IR spectroscopy. All samples show PNIPAM at the surface, indicated by the amide bonds. Figure 2 shows the IR spectra in comparison to usual PNIPAM (not attached to a surface).

All surface coatings show the NH-band around 3300 cm^{-1} and the amide band at 1640 cm^{-1} and 1530 cm^{-1}.The fine structures of the PNIPAM spectra correspond precisely to the spectra of coating (B) and (C), giving evidence that method (B) and (C) are appropriate methods to prepare PNIPAM coated surfaces. Additionally to the PNIPAM bands the spectra of coating (B) and (C) show $Si–CH_3$ and Si–O–Si bands between 1200 cm^{-1} and 900 cm^{-1}. Especially the IR spectra of C approves that the one step coating process with PMSSQ-*b*-PNIPAM is a convenient route to prepare temperature-responsive surfaces. Coating C is comparable to the established grafting-from methods. A difference induced by the PMSSQ block could be found neither in coating (B) nor in coating (C).

To check the temperature-responsive behavior of the surfaces, capillary rise experiments with water of different temperatures have been carried out. The coated glass tubes were placed over a water surface just touching it. The meniscus height was measured as an indication of the surface hydrophobicity. In capillary rise experiments carried out with water at a temperature of 15 °C (below LCST of PNIPAM) the meniscus height in all three samples was measured to be 3.8 cm, indicating a hydrophilic surface. The error of the measurement was ±0.2 cm. Thus, the

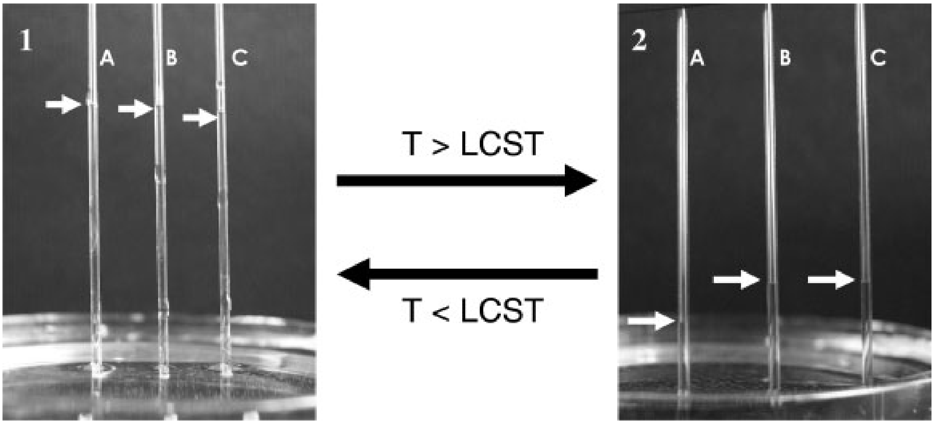


Figure 3.
Capillary rise experiment of PNIPAM coated glass tubes, picture 1: water temperature 15 °C, picture 2: water temperature 40 °C. Tubes A, B and C correspond to the different surface coatings A, B and C.

values of three independent measurements were averaged. When the water was heated at 40°C (above the LCST of PNIPAM) the meniscus height was found to be 1.1 cm in the case of coating (A) and 1.4 cm in the case of coating (B) and (C). Exemplary snapshots of the capillary rise experiments are shown in Figure 3. As a comparison, the meniscus height of an uncoated capillary did not change while changing the water temperature to 40 °C.

The experiment was repeated several times by cooling/heating cycles of the water bath resulting in a rise and fall of the meniscus. In every cycle the previously measured heights of the meniscus were observed without a significant change. For all three surface coatings (A, B and C) a very similar temperature-responsive behavior of the surface was found. Only for surface coating procedure A, a lower meniscus height above LCST was found, which may correspond to a higher population density of PNIPAM chains at the surface due to the higher initiator density during the surface coating procedure.

Overall, using PMSSQ-*b*-PNIPAM polymers as coating materials offers a variety of advantages compared to classical grafting-from techniques. A simple spin- or dip-coating step results in a clean and temperature-responsive surface, avoiding contact of catalysts or other compounds with the surface.

Conclusions

A new method to build up temperature-responsive surfaces was introduced. The successful synthesis of PMSSQ-*b*-PNIPAM gives the possibility to simplify the coating process dramatically. By simple spin-coating or dip-coating procedures a PNIPAM modified surface could be obtained in one step. The synthetic concept to build up functionalized hybrid polymers using the RAFT polymerization carries the potential to incorporate other vinyl monomers in the organic block. For example by using the well known active ester monomers[19] a micro-structured surface pattern could be prepared by μ-contact printing. An analogous surface coating consisting of a active ester layer can be converted by polymer analogues reaction to PNIPAM (with isopropyl amine) but also to other surface modifications are considerable.

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