Synthesis of Functional Inorganic−Organic Hybrid Polymers Based on Poly(silsesquioxanes) and Their Thin Film Properties

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ABSTRACT: New stable and adherent coating materials have been synthesized on the basis of inorganic/organic hybrid polymers. As the inorganic part, different poly(silsesquioxanes) (PSSQ) have been functionalized to act as polymeric chain transfer agents (CTAs) for a reversible addition fragmentation chain transfer polymerization, thereby determining the starting point of a controlled radical polymerization of vinyl-type monomers. Using two different CTAs acrylates, we have successfully polymerized methacrylates and styrene under RAFT polymerization conditions. Different monomers were copolymerized in such an organic block to incorporate multiple functionalities. The variation of the block ratios and the secondary condensation behavior of the inorganic block were investigated. Finally, these materials were used as surface coating materials on silicon, glass, metal, and polymeric substrates. Successful surface functionalization was demonstrated by contact angle measurements. The stability of the film and the adhesion on the substrate were tested in an ISO tape test.

Introduction

Precise control of surface properties is becoming ever more important recently. For example, interfacial interactions have found applications in synthetic systems,[1–6] biological systems,[7] or surface responsive materials.[8] In order to precisely adjust surface properties, different approaches have been explored, all depending on the desired application. Unfortunately, most approaches are not general. Rather they are often adapted only to one specific substrate and one desired property. For example, trichlorosilylalkanes are used to prepare hydrophobic glass surfaces.[9] But they cannot be used to modify for example gold or polymer surfaces. In 2005, Russell and Hawker introduced a first simple strategy to create coatings for a versatile modification of surfaces.[10] Their method is based on cross-linking random organic copolymers. The desired surface properties can be tuned by employing different monomers during the copolymer synthesis. The surface stability is then achieved by cross-linking cyclobutyl groups, resulting in stable and insoluble polymer coatings on surfaces.

Besides organic cross-linkers, inorganic compounds like trifunctional silanes, such as trichlorosilanes, have found broad application in sol−gel chemistry. In addition to the cross-linking ability of trichlorosilanes, they also bind directly to hydroxylated metal oxide surfaces or glass substrates.[11]

Inorganic−organic hybrid materials have received tremendous attention for various applications due to their favorable and often unique combination of properties within one material, which can be used in surface science and other applications. For example, the combination of dyes with triethoxysilanes results in thermally and mechanically stable materials used as waveguides,[12] lasers,[12] sensors,[12] or light emitting diodes.[13] Nanostructured hybrid materials with promising properties, such as low dielectric constant materials for applications in microelectronics[14–16] or superior mechanical properties,[17] have been described. However, to design new materials with desirable and predictable properties, a detailed understanding of structure−property relationships is required.

There are many successful approaches to preparing inorganic/organic hybrid materials containing silica precursors, for example, polymers containing trialkoxysilyl side groups as precursors for sol−gel processing were prepared using RAFT polymerization.[18] Diblock copolymers can be obtained using polymeric PMMA RAFT agents.[19] Polymer−ceramic hybrid materials can also be prepared using appropriate block copolymer and ceramic precursors (ormocers[20]). On the basis of this unique polymer−ceramic interface, unprecedented morphology control on the nanoscale has been obtained. Polyhedral oligomeric silsesquioxanes (POSS, $Si_8O_{12}R_8$) as the smallest molecular silica finds broad application within hybrid materials.[21–23] Polymers can be either grafted to or from POSS.[24–27] Also POSS cubes can be incorporated as side chains.[28] In the work of Wiesner et al., hydrophilic parts of a diblock copolymer were integrated into silica networks,[29] while Clarson et al. investigated the influence of different additives to a bioinspired silification process.[30,31]

Despite the importance of poly(silsesquioxanes) (PSSQs) as emerging materials for low dielectric constant materials in microelectronic devices,[14,15] because of their excellent thermal and electrical properties, their use as coating materials has not been well investigated as yet. The chemical modification of metal oxide surfaces with various organosilanes (R_nSi_{x-4}) has been investigated intensively. In this context, infrared spectroscopy and ^{29}Si NMR spectroscopy have proved to be useful analytical techniques to study the molecular structure. Especially, the binding of organosilanols with surface Si-OH groups and the tendency of mono-, di-, and trifunctional silanols toward surface binding or internal cross-linking were examined.[35–38] Polysilsesquioxanes consist of T1, T2, and T3 branches, which are comparable to mono-, di-, and trifunctional silanols. Thus, they combine the tendency to bind to surface silanols as well as to form networks. To the best of our knowledge, polysilsesquioxanes have not found broad application in the modification of surfaces. However, in conjunction with the versatility of the organic R group, polysilsesquioxanes seem to be ideal candidates to be used as coating materials.[39]

In this paper, we report a versatile surface coating procedure. It is based on a new synthetic concept: applying the RAFT polymerization process to prepare inorganic−organic hybrid polymers, consisting of a poly(silsesquioxane) (PSSQ) inorganic block, which should serve as an adhesion promoter for the substrate as well as a cross-linking unit and an organic block, which should provide the desired surface properties.

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Experimental Part

Materials. All chemicals and solvents were commercially available (Acros Chemicals, ABCR) and used as received unless otherwise stated. All used monomers were distilled under reduced pressure. THF was distilled from sodium/benzophenone under nitrogen.

Instrumentation. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer. ^{29}Si CPMAS NMR spectra were measured on a Bruker DSX 400 MHz FT-NMR spectrometer (rotation = 5000 Hz, T = RT, 4 mm rotor). Chemical shifts (δ) were given in ppm relative to TMS. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to polystyrene standards (PSS). (THF was used as solvent; polymer concentration was 2 mg/mL; column setup was MZ-Gel-SDplus 10^2 Å^2, 10^4 Å^2, and 10^6 Å^2; and the detectors used were refractive index, UV, and light scattering.) Thermogravimetric analysis was performed using a Perkin-Elmer Pyris 6 TGA in nitrogen (10 mg pure polymer in aluminum fan). 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).

All reactions were performed in Argon atmosphere.

Synthesis of *p*-(Chloromethyl)-phenylethyltrichlorosilane (1). *p*-(Chlormethyl)-phenylethyltrichlorosilane was prepared by hydrosilylation reaction of *p*-chloromethylstyrene with trichlorosilane. Platinum on charcoal (100 mg) and 100 mL toluene were placed in a 250 mL round-bottomed flask equipped with a stirring rod, and 75 mmol (10.16 g) trichlorosilane and 50 mmol (7.63 g) *p*-chloromethylstyrene were added to the flask. The reaction mixture was stirred magnetically at 110 °C for 48 h. After filtering over celite, the solvent was removed and the crude product was distilled at 2.5 × 10^{-3} mbar.

Yield: 11.07 g (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). ^{13}C NMR (CDCl$_3$,δ): 141.61, 135.71, 128.91, 128.24, 45.94, 27.91, 25.90. Anal. Calcd: C, 37.52; H, 3.50. Found: C, 38.70; H, 3.73.

Synthesis of p-(Chloromethyl)-phenylethyltrimethoxysilane (2). 35 mmol (9.98 g) *p*-(Chlormethyl-phenylethyltrichlorsilane (1) was dropped in 100 mL methanol (freshly distilled over sodium) in a 200 mL round-bottomed flask equipped with a stirring bar. The mixture was stirred overnight and the solvent was removed afterward on a rotary evaporator.

Yield: 8.44 g (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 (2, 2H); 3.56 (s, 9H); 2.73 (m, 2H); 0.99 (m, 2H). ^{13}C NMR (CDCl$_3$,δ): 144.61, 134.81, 128.54, 128.04, 50.38, 28.35, 11.09. FD mass spectra: 273.9 (100.0%); 274.9 (15.6%); 275.9 (38.9%). Anal. Calcd: C, 52.45; H, 6.97. Found: C, 53.38; H, 7.22.

Synthesis of Dithiobenzoic Acid Benzyl-(4-ethyltrimethoxysilyl) Ester (3). To a solution of 31.6 mmol phenyl magnesium bromide in THF in a 250 mL round-bottomed flask was added 49.7 mmol (3.78 g) of carbon disulfide and stirred magnetically for 15 min at 40 °C. Afterward, 31.7 mmol (8.71 g) of *p*-(chlormethyl)-phenylethyltrimethoxysilane (2) was added, and the solution was stirred at 50 °C for 1 h. The reaction mixture was poured onto ice and the product was extracted with diethyl ether. The ether phase was washed three times with water, dried over MgSO$_4$, and the solvent was removed on a rotary evaporator.

Yield: 9.91 g (25.3 mmol, 79.7%). ^{1}H NMR (CDCl$_3$,δ): 8.01 (m, 1H); 7.27 (m, 8H); 4.53 (d, ^3J = 2.4 Hz, 2H); 3.59 (s, 9H); 2.76 (m, 2H); 1.04 (m, 2H). ^{13}C NMR (CDCl$_3$,δ): 213.79, 144.61, 137.37, 132.26, 129.16, 128.62; 128.21, 128.06, 126.76, 50.41, 42.31, 28.44, 11.10. FD mass spectra: 391.9 (100.0%); 392.9 (26.9%); 393.9 (15.4%); 274.0 (64.6%); 275.9 (38.9). Anal. Calcd: C, 58.13; H = 6.16; S, 16.33. Found: C, 56.20; H, 6.32; S, 16.51.

Synthesis of *p*-(1-Chloroethyl)-styrene (4). Hydrogen chloride was bubbled through 100 mmol 1,4-divinyl benzene in a three neck 250 mL flask during 5 h (approximately 1 bubble per second). The crude product was purified by distillation in vacuum (P = 20 mbar).

Yield: 7.89 g (47 mmol, 47.0%). ^{1}H NMR (CDCl$_3$,δ): 7.52 − 7.26 (m, 4H); 6.78 (dd, $^3J_1$ = 10.8 Hz, $^3J_2$ = 6.6 Hz, 1H); 5.83 (dd, $^3J_1$ = 17.7 Hz, $^3J_2$ = 6.3 Hz, 1H); 5.35 (dd, $^3J_1$ = 11.1 Hz, $^3J_2$ = 5.5 Hz, 1H); 5.14 (quad, ^3J = 6.6 Hz, 1H); 1.90 (d, ^3J = 6.9 Hz, 3H). ^{13}C NMR (CDCl$_3$,δ): 139.31, 137.69, 134.95, 127.24, 125.91, 113.99, 59.07, 25.31. FD mass spectra: 165.9 (100.0%); 166.9 (35.5%); 167.9 (11.8%). Anal. Calcd: C, 72.07; H, 6.65. Found: C, 72.56; H, 6.89.

Synthesis of *p*-(1-Chloroethyl)-phenylethyltrichlorosilane (5). 50 mg platinum on charcoal and 100 mL toluene were placed in a 250 mL round-bottomed flask, and 75 mmol (10.12 g) trichlorosilane and 47 mmol (7.83 g) *p*-(1-chloroethyl)-styrene (4) were then added to the flask. The solution was stirred magnetically at 80 °C for 24 h. After filtration and evaporation of the solvent, the crude product was distilled in high vacuum. Bp. 119 °C at 6 × 10^{-3} mbar.

Yield: 5.88 g (19.5 mmol, 41.4%). ^{1}H NMR (CDCl$_3$,δ): 7.42 − 7.15 (m, 4H); 5.08 (quad, ^3J = 6.9 Hz, 1H); 2.91 (t, ^3J = 6.4 Hz, 2H); 1.85 (d, ^3J = 6.8 Hz, 3H); 1.77 (m, 2H). ^{13}C NMR (CDCl$_3$,δ): 141.02, 138.23, 129.08, 128.37, 59.11, 28.71, 25.73, 21.94. FD mass spectra: 301.9 (100.0%); 300.9 (55.1%); 299.9 (27.9%). Anal. Calcd: C, 39.76; H, 4.00. Found: C, 41.28; H, 4.11.

Synthesis of *p*-(1-Chloroethyl)-phenylethyltrimethoxysilane (6). *p*-(1-Chloroethyl)-phenylethyltrichlorosilane (19.55 mmol, 5.91 g) (5) was added to 100 mL methanol (distilled over sodium) in a 200 mL flask equipped with stirring rod and stirred overnight. The solvent as removed by rotary evaporator.

Yield: 5.28 g (18.3 mmol, 96.3%). ^{1}H NMR (CDCl$_3$,δ): 7.31 − 7.19 (m, 4H); 4.97 (quad, ^3J = 6.8 Hz, 1H); 3.54 (s, 9H); 2.69 (m, 2H); 1.86 (d, ^3J = 6.6 Hz, 3H); 0.96 (m, 2H). ^{13}C NMR (CDCl$_3$,δ): 143.88, 136.26, 128.33, 128.09, 58.04, 51.13, 28.72, 25.50, 11.89. FD mass spectra: 287.9 (100.0%); 288.9 (17.9%); 290.9 (34.0%). Anal. Calcd: C, 54.06; H, 7.33. Found: C, 55.01; H, 7.46

Synthesis of Dithio Benzoic Acid 1-Ethylphenyl-4-(ethyltrimethoxysilyl) Ester (7). To a solution of 25 mmol phenyl magnesium bromide in THF in a 200 mL flask was added 35 mmol (2.66 g) of carbon disulfide and stirred magnetically at 40 °C. After 15 min, 18.3 mmol (5.29 g) *p*-(1-chloroethyl)-phenylethyltrimethoxysilane (6) was added and stirred at 50 °C for 1 h. The reaction mixture was poured onto ice and extracted with diethyl ether. The organic phase was washed with water, dried over MgSO$_4$, and the solvent was removed by rotary evaporator.

Yield: 5.13 g (12.63 mmol, 69,0%). ^{1}H NMR (CDCl$_3$,δ): 8.08 (m, 1H); 7.31 − 7.19 (m, 8H); 4.41 (quad, ^3J = 6.5 Hz, 1H); 3.54 (s, 9H); 2.80 (m, 2H); 1.74 (d, ^3J = 6.6 Hz, 3H); 0.92 (m, 2H). ^{13}C NMR (CDCl$_3$,δ): 217.02, 142.44, 139.12, 135.55, 131,01, 129.04, 128.99, 127.85, 127.00, 52.11, 43.24, 27.16, 20.37, 12.40. FD mass spectra: 405.9 (100.0%); 406.9 (34.5%); 404.9 (20.3%); 289.9 (60.8%). Anal. Calcd: C, 59.07; H, 6.44; S, 15.77. Found: C, 58.79; H, 6.81; S, 13.29.

Synthesis of *p*-Hydroxy Benzophenone Acrlyate (8). *p*-Hydroxy benzophenone (50 mmol, 9.91 g) and 30 mL chloroform were placed in a 100 mL round bottomed flask. To the flask was then added first 50 mmol (5.06 g) of triethyl amine and afterward 100 mmol (9.05 g) of acryloyl chloride. The reaction mixture was stirred at room temperature for 2 h, washed with water, and dried over $MgSO_4$. After removing the solvent, the crystalline product was recrystallized from hexane.

Yield: 9.87 g (39.16 mmol, 78.3%). ^{1}H NMR ($CDCl_3$,δ): 7.84 (d, ^3J = 8.4 Hz, 2H); 7.78 (d, ^3J = 7.2 Hz, 2H); 7.46 (t, ^3J = 17.4 Hz, 1H); 7.44 (t, ^3J = 7.2 Hz, 2H); 7.25 (d, ^3J = 8.4 Hz, 2H); 6.61 (d, ^3J = 17.4 Hz, 1H); 6.32 (dd, $^3J_1$ = 17.4 Hz, $^3J_2$ = 10.4 Hz, 1H); 6.04 (d, ^3J = 10.5 Hz, 1H). ^{13}C NMR ($CDCl_3$,δ): 195.42, 163.92, 153.82, 137.46, 135.06, 133.28, 132.46, 131.64, 129.92, 128.33, 127.54, 121.49. FD mass spectra: 252.2 (100.0%); 253.2 (16.23%). Anal. Calcd: C, 76.18; H, 4.76. Found: C, 75.95; H, 4.74.

Synthesis of *p*-Hydroxy Benzophenone Methacrlyate (9). Preparation similar to (8). Yield: 9.48 g (35.61 mmol, 71.2%). ^{1}H NMR ($CDCl_3$,δ): 7.84 (d, ^3J = 8.4 Hz, 2H); 7.76 (d, ^3J = 7.2 HZ, 2H); 7.53 (t, ^3J = 7.2 Hz, 1H); 7.45 (t, ^3J = 7.2 Hz, 2H); 7.23 (d, ^3J = 8.4 Hz, 2H); 6.35 (s, 1H); 5.77 (s, 1H); 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$,δ): 195.53, 165.29, 154.21, 137.51, 135.54, 134.95, 132.55, 131.66, 129.93, 128.32, 127.89, 121.57, 18.31. FD mass spectra: 266.2 (100.0%); 267.2 (18.2%). Anal. Calcd: C, 76.68; H, 5.30. Found: C, 75.99; H, 5.12.

Synthesis of PSSQ Macro RAFT Agents. The PSSQ macro initiators have been synthesized following a general procedure. The desired trifunctional silane and the functionalized RAFT agent were added in the molar ratio 20:1 in a 200 mL flask. Then 20 mL THF, 1000 mol % water, and 3 mol % HCl were injected. The solution was stirred magnetically at 0 °C for 3 h, then diluted with diethyl ether, washed with water, and dried over $MgSO_4$. The solvent was evaporated, and the product was dried in high vacuum (1×10^{-3} mbar).

PMSSQ Macro RAFT Agent 1 (MI-1) by Reaction of Methyltrimethoxy Silane with (3). ^{1}H NMR (THF-d_8, δ): 7.99 (br,5H); 7.36 (br, 2H); 7.20 (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). ^{29}Si CPMAS NMR (δ): −48.27 (T1); −57.41 (T2); −66.47 (T3). M_n = 4990 g/mol, PDI = 1.63

PMSSQ Macro RAFT Agent 2 (MI-2) by Reaction of Methyltrimethoxy Silane with (7). ^{1}H NMR (acetone-d_6, δ): 7.63 − 7.15 (br, 9H); 5.26 (br, 2.1H); 3.61 (br, 1H); 2.88 (br, 2H); 1.77 (br, 3H); 1.07 (br, 2H); 0.16 (br, 69.1H). ^{29}Si CPMAS NMR: δ(ppm) = −48.88 (T1); −57.90 (T2); −65.29 (T3). M_n = 3210 g/mol, PDI = 1.78.

PODSSQ Macro RAFT Agent (MI-3) by Reaction of Octadecyltrichloro Silane with (3). ^{1}H NMR (THF-d_8, δ): 7.20 (br, 9H); 4.98 (br); 4.10 (br, 2H); 3.53 (br); 2.50 (br, 2H); 1.65 (br, 2H); 1.30 (br); 0.95 (br); 0.63 (br). M_n = 4213 g/mol, PDI = 1.73.

PFOSSQ Macro RAFT Agent (MI-4) by Reaction of 1H,1H,2H,2H-Perfluoroctyltrichloro Silane with (3). ^{1}H NMR (THF-d_8, δ): 7.21 (br, 9H); 4.60 (br); 4.03 (br, 2H); 3.60 (br, 2H); 2.75 (br, 2H); 2.30 (br); 1.74 (br, 2H); 0.95 (br). M_n = 9339 g/mol, PDI = 3.00.

PPSSQ Macro RAFT Agent (MI-5) by Reaction of Phenyltrimethoxy Silane with (3). ^{1}H NMR ($CDCl_3$, δ): 7.65 − 7.01 (br); 5.18 (br); 4.47 (br, 2H); 3.50 (br); 1.77 (br, 2H); 1.19 (br, 2H). M_n = 4600 g/mol, PDI = 2.00.

POSSQ Macro RAFT Agent (MI-6) by Reaction of Octyltrichloro Silane with (3). ^{1}H NMR ($CDCl_3$, δ): 8.04 − 7.46 (br, 9H); 4.68 (br, 2H); 3.61 (br); 1.50 − 0.63 (br). M_n = 5070 g/mol, PDI = 1.80.

RAFT Polymerization. Inorganic−organic hybrid polymers were prepared by RAFT polymerization. A general procedure is as follows. The macro RAFT agent (0.5 g), 10 mg AIBN, 4 mL dioxane, and a defined amount of monomer (usually 2 g unless otherwise stated) were placed in a 20 mL Schlenk flask, degassed, and stirred magnetically at 80 °C for 4 h in Ar atmosphere. The resulting polymer was precipitated in *n*-hexane and dried in high vacuum (1×10^{-3} mbar).

PMSSQ-PMA Using MI-1. ^{1}H NMR ($CDCl_3$, δ): 3.63 (br, 3H); 2.29 (br, 1H); 1.66 (br, 2H); 0.16 (br, 0.55 H). ^{29}Si CPMAS NMR (δ): = −57.80 (T2); −66.92 (T3). M_n = 28100 g/mol, PDI = 2.2. Yield: 1.97 g.

PMSSQ-PEHA Using MI-1. ^{1}H NMR ($CDCl_3$, δ): 4.81 (br, 0.1H); 3.93 (br, 2H); 2.32 (br, 1H); 1.85 (br, 1H); 1.58 (br, 2H); 1.29 (br, 8H); 0.99 (br, 6H); 0.17 (br, 0.7H). M_n = 33500 g/mol, PDI = 1.9. Yield: 1.35 g.

PMSSQ-PMMA Using MI-2. ^{1}H NMR ($CDCl_3$, δ): 5.02 (br, 0.1H); 3.59 (br, 3H); 1.81 (br, 2H); 1.34 (br, 3H); 0.16 (br, 0.8H). ^{29}Si CPMAS NMR (δ): −58.23 (T2); −67.10 (T3). M_n = 28930 g/mol, PDI = 1.5. Yield: 1.96 g.

PMSSQ-PDMA Using by MI-2. ^{1}H NMR ($CDCl_3$, δ): 5.06 (br, 0.1H); 4.00 (br, 2H); 1.90 − 1.72 (br, 16H); 1.27 (br, 3H); 1.10 − 1.01 (br, 3H); 0.15 (br, 1.3H). M_n = 25520 g/mol, PDI = 2.4. Yield: 2.19 g.

PMSSQ-PS Using MI-1. ^{1}H NMR ($CDCl_3$, δ): 7.10 (br, 5H); 4.55 (br, 0.1H); 2.34 (br, 1H); 1.25 (br, 2H); 0.16 (br, 1.2H). M_n = 29840 g/mol, PDI = 2.9. Yield: 2.11 g.

PMSSQ-PS Using MI-2. ^{1}H NMR ($CDCl_3$, δ): 7.10 (br, 5H); 5.10 (br, 0.1H); 2.40 (br, 1H); 1.33 (br, 2H); 0.17 (br, 1.4H). M_n = 23000 g/mol, PDI = 2.7. Yield: 2.30 g.

PPSSQ-PMA Using MI-5. ^{1}H NMR ($CDCl_3$, δ): 7.22 (br, 1.7H); 3.66 (br, 3H); 2.29 (br, 1H); 1.68 (br, 2H). M_n = 35890 g/mol, PDI = 1.98. Yield: 1.77 g.

PPSSQ-PEHA Using MI-5. ^{1}H NMR ($CDCl_3$, δ): 7.25 (br, 1.6H); 3.89 (br, 2H); 2.26 (br,1H); 1.92 (br, 1H); 1.55 (br, 2H); 1.33 (br, 8H); 0.95 (br, 6H). M_n = 33200 g/mol, PDI = 1.68. Yield: 1.57 g.

POSSQ-PMA Using MI-6. ^{1}H NMR ($CDCl_3$, δ): 3.68 (br, 3H); 2.28 (br, 1H); 1.65 (br, 2H); 1.45 − 0.60 (br, 6H). M_n = 32900 g/mol, PDI = 1.99. Yield: 1.40 g.

POSSQ-PEHA Using MI-6. ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.69 (br, 2H); 2.28 (br, 1H); 1.95 (br, 1H); 1.60 (br, 2H); 1.45 − 0.60 (br, 5.2H). M_n = 27000 g/mol, PDI = 1.82. Yield: 1.52 g.

PODSSQ-PMA Using MI-3. ^{1}H NMR ($CDCl_3$, δ): 3.70 (br, 3H); 2.30 (br, 1H); 1.64 (br, 2H); 1.31 (br, 18H); 0.90 (br, 1.6H); 0.60 (br, 1H). M_n = 37090 g/mol, PDI = 1.92. Yield: 1.44 g.

PODSSQ-PEHA Using MI-3. ^{1}H NMR ($CDCl_3$, δ): 3.70 (br,2H); 2.20 (br, 1H); 1.97 (br, 1H); 1.60 (br, 2H); 1.31 (br, 18H); 0.97 − 0.90 (br, 1.6H); 0.60 (br, 1H). M_n = 35200 g/mol, PDI = 1.74. Yield: 1.30 g.

PFOSSQ-PMA Using MI-4. ^{1}H NMR ($CDCl_3$, δ): 3.68 (br, 3H); 2.28 (br, 1H); 2.20 (br, 1.4H); 1.65 (br, 2H); 0.90 (br, 1.4H). M_n = 22000 g/mol, PDI = 1.74. Yield: 1.48 g.

PFOSSQ-PEHA Using MI-4. ^{1}H NMR ($CDCl_3$, δ): 3.69 (br, 3H); 2.20 (br, 2.1H); 1.95 (br, 1H); 1.60 (br, 2H); 0.97 − 0.90 (br, 1.1H). M_n = 24560 g/mol, PDI = 1.60. Yield: 1.20 g.

PMSSQ-PMA Containing 5 mol % (8). ^{1}H NMR ($CDCl_3$, δ): 7,80 − 7,24 (m, H1, 0,3H), 3,67 (br, H2, 3H), 2,30 (br, H3, 2H), 1,67 (br, H4, 1H), 0,13 (br, H5, 1,2H). Mn = 37480 g/mol, PDI = 1,22.

PMSSQ-PMMA Containing 5 mol % (9). ^{1}H NMR ($CDCl_3$, δ): 7,85− 7,17 (m, H1, 0,35H), 3,68 (br, H2, 3H), 1,79 (br, H3, 2H), 1,24 − 0,81 (br, H4, 3H), 0,14 (br, H5, 1,2H). M_n = 22310 g/mol, PDI = 1,65.

(Signals coming from the initiating units and integrations are not considered here, because of the small values compared to the polymer signals.)

Results and Discussion

A polymeric precursor for a versatile surface coating material must fulfill a number of different requirements. Basically, general coating systems must satisfy two main requirements: first, film stability and adhesion to the substrate of choice must be effective, and second, a simple method for surface functionalization and modification is highly desirable. An inorganic–organic hybrid polymer based on poly(silsesquioxanes) (PSSQ) as an inorganic block and an organic block composed of simple vinyl monomers should offer potential to develop a variety of surface coating materials with well-defined but tailorable properties.

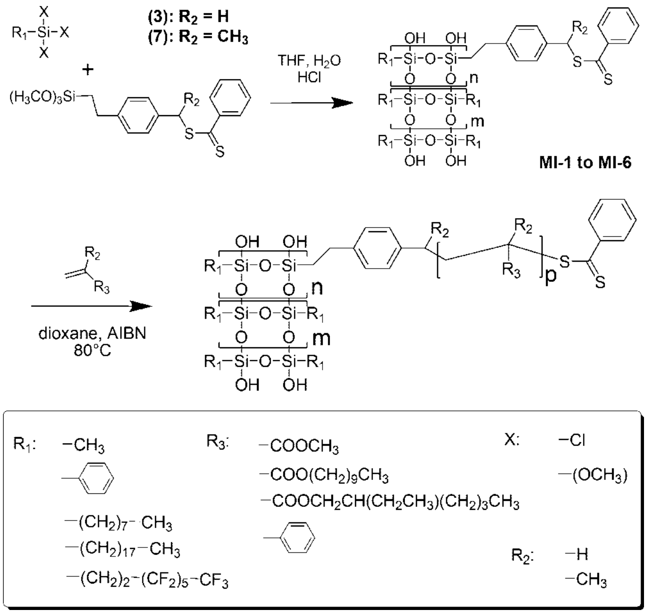
The synthetic concept presented here consists mainly of two parts. First, a PSSQ ($RSiO_{1.5}$) macro chain transfer agent (CTA) is synthesized, consisting of the desired silsesquioxane [e.g.methyltrimethoxy silane to synthesize poly(methyltrimethoxysilane) (PMSSQ)] and a functional moiety that follows control of RAFT polymerization of vinyl monomers yielding an organic polymer block. The method of choice, for preparing inorganic/organic hybrid materials is a controlled radical polymerization not only due to the possibility to obtain low polydispersities but also mostly due to the fact that the polymer chain grows only from a defined site (grafting point).

Atom transfer radical polymerization (ATRP) of methyl methacrylate initiated by functionalized PMSSQ macro initiators using usual ATRP conditions has been described previously.[16,32] Further the reversible addition–fragmentation chain transfer (RAFT) polymerization offers an excellent opportunity to control radical polymerization and to initiate the radical polymerization from a defined site, in our case from PSSQ macro chain transfer agents. In sum, the synthetic pathway begins with the synthesis of trimethoxysilyl-functionalized dithioesters as the CTA for the RAFT process. Then, these CTAs are cocondensed with methyl trimethoxysilane (MTMS) or other trialkoxy silanes to build up PSSQ macro CTAs.

In the last step, the polymerization of the desired monomer controlled by the macro CTA results in the formation of the organic polymer chains attached onto the PMSSQ block. Scheme 1 visualizes the synthetic concept, which features a high variability: easy modification of the inorganic block or the organic block, adjustability of the block ratio, and the variable amount of initiating sites in the PSSQ macro CTA resulting in different numbers of organic chains on one inorganic block. In the following, the resulting flexibility of the synthesis will be discussed in detail.

Synthesis of PMSSQ Macro CTA. The CTA must be able to be cocondensed into a PSSQ and to regulate the controlled radical polymerization. Cocondensation is achieved by hydrolysis of a trimethoxy silyl group. To keep the variability as high as possible, it is desired to polymerize acrylates, methacrylates, and styrene based monomers. Thus, two different CTAs were synthesized to mimic the growing chain end of acrylates and methacrylates, respectively. The obtained CTAs dithiobenzoic acid benzyl-(4-ethyltrimethoxysilyl) ester (3) and dithio benzoic acid 1-ethylphenyl-4-(ethyltrimethoxysilyl) ester (7) are shown in Scheme 1. The overall yield to (3) was 54%, and in case of (7) the yield was 13%. The low overall yield resulted from the low yield of the purification after the first step. It was expected that (3) can be used in the polymerization of acrylates and styrene, while (7) should be applicable for methacrylates. Overall, this should cover a wide spectrum of vinyl-type monomers to be used for the synthesis of hybrid polymers.

Scheme 1. Synthetic Pathway Toward PSSQ Based Hybrid Polymers[a]



[a] The first steps shows the cocondensation of the macro-CTA, and the second step shows the grafting from polymerization via RAFT to yield an inorganic/organic hybrid polymer.

Table 1. Properties of the Different Macro-CTA in Dependence of Cocondensation Conditions

macro initiator	initial molecular ratio	M_n (g/mol)	PDI	initiator ratio after cocondensation	m/n[a]	IPM[b]
MI-1	20:1	4990	1.63	23:1	11	4.4
MI-2	20:1	3210	1.78	23:1	11	3.0
MI-3	20:1	4213	1.73	16:1	8	1.2
MI-4	20:1	9339	3.00	16:1	8	4.1
MI-5	20:1	4600	2.00	15:1	7	3.4
MI-6	20:1	5070	1.80	13:1	6	3.4

[a] Ratio between pure PSSQ rungs and initiator rungs in an assumed ladder like structure of the macro initiator. [b] IPM (initiating groups per molecule): calculated average number of initiating groups per PMSSQ macro initiator derived from integral ratio of ^{1}H NMR spectra.

A cocondensation step is then used to generate soluble PSSQ macro CTAs, which can be used in a subsequent polymerization. To show the versatility of the concept, different polymeric CTAs were synthesized based on PSSQ. Dithiobenzoic acid benzyl-(4-ethyltrimethoxysilyl) ester (3) and dithio benzoic acid 1-ethylphenyl-4-(ethyltrimethoxysilyl) ester (7) were cocondensed with MTMS to yield the macro CTAs MI-1 and MI-2, respectively. With both macro CTAs in hands, it should be possible to investigate the different chain transfer behavior during the polymerization leading to the polymerization of either acrylates or methacrylates and styrenes.

To demonstrate the flexibility of the PSSQ system, other trialkoxy silanes or trichlorosilanes were also used in the synthesis of macro CTAs, yielding MI-3 to MI-6, possessing the same CTA site (dithiobenzoic acid benzyl-(4-ethyltrimethoxysilyl) ester (3)) but different organic moieties on the PSSQ. To compare the effect of different substituted PSSQs octyl- and octadecyl-trichloro silanes (MI-6 and MI-3, respectively) were used during the cocondensation. Phenyl trimethoxy silane and 1H,1H,2H,2H-perfluorooctyltrichloro silane (yielding MI-4 and MI-5, respectively) were used to investigate the influence of aromatic or fluorinated sidechains and also to show potential to incorporate functional groups in the inorganic block. All mentioned trialkoxy- or trichloro-silanes could be converted

Table 2. Thermogravimetric Analyses of PMSSQ−PEHA (Grafted from MI-1) and PMSSQ−PMMA (Grafted from MI-2)

hybrid polymer	macro-CTA	amount macro-CTA (g)	amount monomer (g)	expected wt ratio organic:inorganic	wt ratio by TGA organic:inorganic
PMSSQ−PEHA-1	MI-1	0.5	0.50	50:50	60:40
PMSSQ−PEHA-2	MI-1		1.00	67:33	75:25
PMSSQ−PEHA-3	MI-1		1.50	75:25	88:12
PMSSQ−PEHA-4	MI-1		2.00	80:20	92:8
PMSSQ−PEHA-5	MI-1		2.50	83:17	94:6
PMSSQ−PMMA-1	MI-2	0.5	0.50	50:50	46:54
PMSSQ−PMMA-2	MI-2		1.00	67:33	61:39
PMSSQ−PMMA-3	MI-2		1.50	75:25	79:21
PMSSQ−PMMA-4	MI-2		2.00	80:20	85:15
PMSSQ−PMMA-5	MI-2		2.50	83:17	86:14

into PSSQ macro CTAs. The molecular weights of all different macro CTAs varied between 3 000 and 10 000 g/mol (see Table 1), and all of them were soluble in common organic solvents, such as dioxane, THF, acetone, and ethylacetate. Dioxane was then used as the solvent in the following controlled radical polymerization.

The incorporation of the CTA sites in the PSSQ polymers was determined by ^{1}H NMR spectroscopy and compared with the initial molecular ratios (see Table 1). The initial molecular ratio was determined by the ratio of CTA sites to the number of regular side groups. The remaining reactivity in the form of silanol groups (Si−OH) of the inorganic block was determined by $^{29\mathrm{Si}}$ solid state NMR spectroscopy for MI-1 and MI-2. The spectra are shown in Figure S1 of Supporting Information. Both of them show T1- and T2- branches, indicating a highly reactive polysilsesquioxanes.

Polymerization. In the next step, the macro CTAs were used as starting points for radical polymerization under RAFT conditions, resulting in hybrid organic/inorganic copolymers. First, the polymerization behavior of the different CTA species was determined. Due to the different chemical architectures of the polymeric CTAs (3) and (7), MI-1 is expected to polymerize acrylates while MI-2 should polymerize methacrylates. No influence should be detected on the polymerization of styrene. Both macro CTAs were used in the polymerization of methyl acrylate (MA), ethyl hexyl acrylate (EHA), methyl methacrylate (MMA), decyl methacrylate (DMA), and styrene (S). The obtained polymers were characterized using ^{1}H NMR spectroscopy and gel permeation chromatography (GPC) (see Table S1, Supporting Information). For MI-1, inorganic/organic hybrid polymers were obtained with MA, EHA, and S. MI-2 yielded organic/inorganic hybrid polymers using MMA, DMA, and styrene. In all other cases no hybrid polymer could be obtained after work up. The different macro CTAs were able to yield inorganic/organic hybrid polymers consisting of PMSSQ as an inorganic block and polyacrylate, polymethacrylate or polystyrene as an organic block. Both, MI-1 and MI-2 could be used to initiate the polymerization of styrene. No advantage of one of these CTAs over the other in regard to the polymerization of styrene could be found. Both yields and molecular weights were in comparable range.

The other PSSQ macro CTAs, carrying octadecyl- (MI-3), 1H,1H,2H,2H-perfluorooctyl- (MI-4), phenyl- (MI-5) or octyl- (MI-6) sidegroups, were tested in analogous polymerization reactions. As MI-3−MI-6 are based on the CTA site (3), only the polymerization of acrylates was considered. POSSQ, PODSSQ, PFOSSQ, and PPSSQ based macro CTAs initiated the polymerization of MA and EHA, proving that the concept of synthesizing inorganic/organic hybrid polymers can easily be varied in the inorganic part as well as in the organic part. In all cases, GPC measurements showed a monomodal peak for the hybrid polymers with reasonable PDIs between 1.2 and 3, considering the step growth process of trifunctional monomers in the inorganic block (Table S1, Supporting Information). Achieved molecular weights were in the range between 22 000 and 40 000 g/mol, very similar to the corresponding PMSSQ based hybrid polymers. Again, a significant difference in the polymerization behavior of the different macro CTAs was not found. A collection of all synthesized hybrid polymers can be found in the Supporting Information.

To compare the ratios of the inorganic and the organic blocks with the initial ratios of macro CTA to organic monomer, the obtained PMSSQ−PEHA and PMSSQ−PMMA hybrid polymers were analyzed by TGA. An exemplary TGA for both polymers is given in the Supporting Information, Figure S3. For both polymers, the secondary condensation of the inorganic block occurred between 100 and 150 °C, indicating cross-linking, while around 400 °C, the decomposition of the organic block could be detected. The ratio of decomposed mass to remaining mass was compared with the initial molecular ratio and the results are summarized in Table 2. In all cases, the block ratio could be adjusted by tuning the desired ratio between inorganic macro CTA and organic monomer.

For a material to cross-link and form a stable film or bind to hydroxylated surfaces, the inorganic block must possess sufficient reactive groups in the form of silanol functionalities after the polymerization of the organic monomer. Again, the remaining reactivity of the inorganic block was investigated by ^{29}Si CPMAS NMR spectroscopy. In Figure 1, the $^{29\mathrm{Si}}$ CPMAS NMR spectra of PMSSQ−PMMA after cocondensation, after polymerization, and after curing at 130 °C for 3 h are compared. The decrease of T1- and T2-branches after polymerization are most likely due to the 80 °C polymerization temperature, inducing slight condensation. Nevertheless, after polymerization of the organic monomer, the inorganic block still retained reactive silanol groups, which guarantee cross-linking or binding by secondary condensation afterward. In the case of PMSSQ−PMA and PMSSQ−PMMA, around 40% of all silicon branches were T1 or T2 branches, ensuring enough reactive silanol groups.

The presented synthetic concept offers many possibilities to tune the desired properties of an inorganic/organic coating

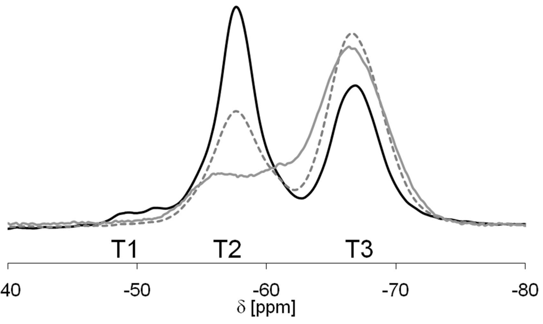
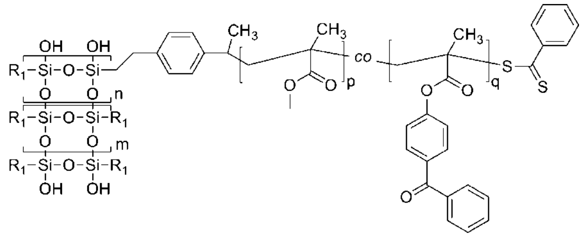


Figure 1. ^{29}Si CPMAS NMR spectra of (a) MI-2 (black solid line), (b) PMSS–QPMMA after polymerization (gray dashed line), and (c) PMSSQ–PMMA after curing (130 °C, 3 h) (gray solid line).

Scheme 2. Structure of the Hybrid Polymer PMSSQ−PMMA, Which Contained 5 mol % of a Photocross-Linkable Benzophenone Moiety



material by allowing the incorporation of different functions or monomers in the inorganic as well as the organic block and by adjusting the block ratio between both blocks. However, for some applications, it is desired to incorporate more than one function in the organic block. This can be achieved by a statistical copolymerization of two monomers during the polymerization step. As an example, a second monomer, *p*-hydroxy benzophenone (meth)acrylate (8/9), was copolymerized with MA or MMA in the presence of polymeric CTA MI-1 or MI-2. As an exemplary, the chemical structure of the hybrid polymer PMSSQ-PMMA, which contains 5 mol % of a photocross-linkable benzophenone moiety, is shown in Scheme 2. By use of the approach described above, 5 mol % of (8) or (9) were added in the monomer feed, respectively. Again, ^{1}H NMR spectroscopy and GPC were used to characterize the obtained hybrid polymers. The ^{1}H NMR spectrum of PMSSQ−PMMA containing 5 mol % of (9) is shown in Figure 2. Clearly, the expected peaks for the benzophenone moiety between 7 and 8 ppm can be seen. The incorporation of the benzophenone groups was also proved by irradiation with UV light (UV-A). Benzophenone is known to react as a UV cross-linker.[33] After 20 min irradiation of a 10 wt % solution of the PMA or PMMA hybrid polymers containing 5 wt % (8) or (9) with UV-A light, gelation occurred. Figure S2 in the Supporting Information shows a GPC of a PMSSQ−PMMA hybrid polymer with 5 mol % (9) before and after 5 min irradiation (sample in THF solution, 2 mg/mL). Further irradiation resulted in an insoluble polymer (solubility checked in chloroform, THF, and ethylacetate).

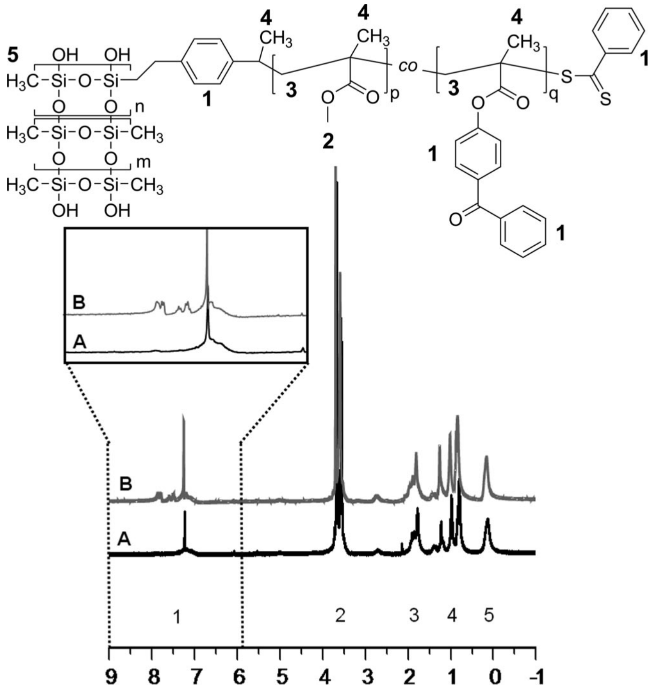


Figure 2. ^{1}H NMR spectra of PMSSQ−PMMA (A), $q = 0$ and PMSSQ−PMMA containing 5% of (9) (B), $q = 0.05$.

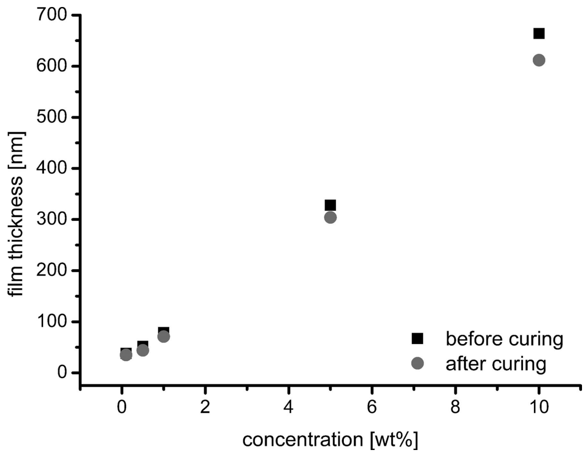


Figure 3. Film thicknesses of PMSSQ−PMMA hybrid films on silicon wafers measured by ellipsometry before and after curing (error range ± 5nm).

These experiments indicate that by random copolymerization of different monomers additional functions or properties can be incorporated in the organic block. In this case, organic/inorganic hybrid materials were obtained, which provide cross-linking either by the secondary condensation of the inorganic block by heating or by photocross-linking of the organic block. These materials are supposed to lead to an understanding of film forming properties of inorganic/organic hybrid polymers, because the inorganic secondary condensation of a film can be initiated either in the presence of a flexible organic moiety or a rigid UV-cross-linked organic matrix, which may yield in a different molecular structure within the film. Beside this academic approach, the possibility of photocross-linking can also be used to pattern the film or to attach other materials on top of surface coatings by UV irradiation.

Surface Coatings. To determine the utility of these hybrid materials as surface coatings, thin films on different substrates were prepared via spin-coating from a solution in THF with 4000 rpm for 15 s resulted in stable and transparent films (spin coated from 0.1−10 wt % solution in THF). The dependence of the film thickness from the concentration of PMSSQ-PMMA in THF is shown in Figure 3. As expected, a linear behavior between concentration and thickness was found. Thinner film thicknesses were obtained for cured films compared to uncured films most likely due to the loss of mass in the secondary condensation step.

As described in the introduction, ideal coating materials should be applicable on a wide range of substrates, i.e., stable and adherent films should be formed on any surface type. Different hybrid polymers were spin coated from a 10 wt % solution in THF as described above on silicon, glass, steel, copper, polycarbonate, and poly(methyl methacrylate) surfaces. The successful surface coating of the substrate was analyzed by contact angle measurement and the results are summarized in Table 3. While the advancing contact angles of water on different substances vary dramatically, depending on the nature of the material, all surfaces showed after coating with the respective hybrid polymers similar advancing contact angles. In other words, the contact angle is determined only by the hybrid coating agent used and not by the substrate, indicating not only a successful surface modification but also the potential of hybrid polymers as coating materials. The obtained contact angles change depending on the chemical compositions of the hybrid polymer. The highest contact angles could be measured for PSOSSQ−PMA, with contact angles well above 120°. Clearly, this high contact angle is due to the influence of the perfluorinated chains. The lowest contact angles were found for

Table 3. Contact Angles of Different Surface Coatings on Different Substrates (Hybrid Polymers were Spin Coated from 10 wt % THF Solution and Cured at 130 °C for 1h)[a]

	advancing contact angle (deg)					
hybrid polymer	Si	glass	steel	copper	PC	PMMA
without coating	42	9	92	114	98	70
PMSSQ-PMA	108	104	102	104	107	106
PPSSQ-PMA	92	91	92	96	91	91
POSSQ-PMA	112	110	111	110	117	123
PODSSQ-PMA	120	115	110	116	119	118
PFOSSQ-PMA	129	130	127	125	128	123

[a] Average value of 20 individual measurements, error range ± 3°.

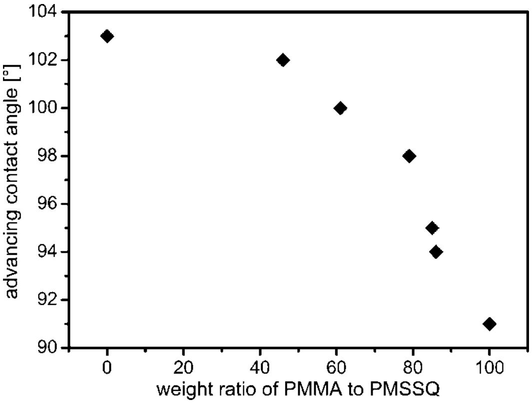


Figure 4. Influence of the variation of the organic to inorganic weight ratio on the observed contact angle after spin coating on a silicon substrate (spin-coated from 10 wt % solution in THF).

PPSSQ−PMA, with contact angles above 90°, which can be assigned to the nature of the phenyl subsitutents.

The influence of the inorganic/organic ratio of the hybrid polymer on the observed contact angle was measured using the different PMSSQ−PMMA hybrids, as summarized in Table 2. The weight ratio of the PMMA fraction was varied from 46 to 86%. As shown in Figure 4, the observed contact angle showed a nonlinear transition from 103° (pure PMSSQ) to 91° (pure PMMA). This nonlinear behavior indicated that the composition on the surface does not necessarily match with the bulk composition of the hybrid polymer and is rather dominated by the fraction of lower surface energy, in this case PMSSQ. A similar trend was also found for POSSQ−PMA coatings.

The stability of the film and the adhesion on the substrate was tested using an ISO tape test.[34] The tested surfaces were classified using the classification given in ISO standard procedure, i.e., 0 indicates absolute no tearing, and 5 indicates a detachment of more than 50% coating material (see Table S2, Supporting Information). Before curing, all surface coatings could easily be detached from the surface. After the thermal cross-linking of the hybrid polymer thin films, all coatings showed a complete adhesion independent of the tested substrate, thereby proving their potential use as robust coating materials.

Conclusions

New organic/inorganic hybrid polymers were prepared using RAFT polymerization as a key process to link organic polymers with an inorganic precursor polymer. Two different RAFT agents were prepared. Both of them could be incorporated in a soluble silsesquioxane macro CTA. A wide spectrum of vinyl-type monomers could be polymerized into the organic block by tuning the molecular architecture of the polymeric CTAs. To enlarge the functionality of the organic block random copolymerization was also investigated. As an example, UV cross-linkable monomers could be incorporated in the hybrid polymer. It is possible to control the block ratios between inorganic and organic blocks by adjusting the initial ratio of macro initiator and organic monomer before polymerization. The flexibility in the synthesis of the inorganic block was shown by using different trifunctionalized monomers in the cocondensation step to build up different macro initiators. The inorganic block can be tuned toward many properties by condensing the desired monomers. The used silsesquioxane has no significant influence on the following polymerization. PMA and PEHA hybrid polymers could be obtained from alkyl-, aryl-, or fluorinated alky-substituted macro initiators. These experiments prove the high variability of the synthetic concept to build up hybrid materials. The properties in the inorganic and the organic block can be adjusted easily. An easy control of the block ratio could be proved by thermogravimetrical measurements. As these materials are supposed to be used as coating materials their ability to cross-link was determined by silicon solid state NMR techniques. After the polymerization, usually more than 30% of the silicon branches are still able to undergo a secondary condensation and so guarantee a cross-linking or bonding to metal or metal oxide substrates. Surface coatings could be processed on a wide range of different substrates. A successful surface functionalization could be determined via contact angle measurements. Beside silicon and glass wafers metals like steel and copper as well as polymeric surfaces like PMMA or PC could be coated very stable. The concept presented in this paper to produce highly variable hybrid polymers but still having enough reactivity to fully cross-link, seems to fulfill the requirements on an ideal coating material.

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Supporting Information Available: ^{29}Si CPMAS NMR spectra of macro initiator 1 (MI-1) and macro initiator 2 (MI-2), molecular weight distributions of PMSSQ-PMMA containing 5% of (9), a list of synthesized polymers, and the tape test results. This information is available free of charge via the Internet at http://pubs.acs.org.

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