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Synthesis of Poly(styrene) Monolayers Attached to High Surface Area Silica Gels through Self-Assembled Monolayers of Azo Initiators

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ABSTRACT: We report on the radical-chain polymerization of styrene using self-assembled monolayers of azo initiators covalently bound to high surface area silica gels. In this process monolayers of poly(styrene) molecules terminally attached to the surface of the inorganic substrate are obtained. As the initiator molecules are immobilized at the surfaces in a one-step reaction, well-reproducible layers can be prepared and the surface concentration of the initiator can be adjusted in a wide range between the limit of detection and full surface coverage. In the subsequent polymerization reactions polymer monolayers with high, controlled graft density can be obtained. The synthesis of the attached layers and the characterization by X-ray photoelectron spectroscopy, diffuse reflectance infrared spectroscopy (DRIFT), and elemental analysis are described. After cleavage of an ester group that connects the polymers to the surface, the molecular weights of the polymers were determined. The results of the study show that this "grafting from" technique can be used for the preparation of polymer layers with controlled, high graft densities.

Introduction

In order to tailor the surface properties of inorganic materials (e.g., silica gels, silicon wafers), ultrathin films have been prepared from a large variety of polymers.^{1–4} Most systems described up to now are based on the physisorption of either homopolymers or block copolymers with a short block interacting with the surface, the other being only weakly absorbed.⁴ However, the interaction between the polymer and the surface is usually not so strong as it is in most cases only caused by van der Waals forces or is due to hydrogen bonding. Therefore, desorption can occur upon exposure to a good solvent or the polymer can be displaced by other polymers or low molecular weight compounds present in the ambient, which compete for adsorption sites at the surface. The decrease in the interaction between the polymer and the substrate due to the displacement of the polymer molecules, however, leads to strong changes in the physical properties of the layers.

Furthermore, the obtained films are often thermally unstable due to the low interaction between the polymer and the solid substrate. Upon heating the ultrathin polymer films to temperatures above the glass transition temperature (or melting point), dewetting is observed.^{5,6} The continuous ultrathin film is broken up, droplets of the polymer form, and the surface is no longer homogeneously covered.

A much stronger adhesion between the polymer chains and the substrate is achieved if the macromolecules are covalently bound to the surface. To establish a chemical bond between the chain end of the polymer molecules and the surfaces, often end-functionalized polymers were synthesized and reacted with appropriate

surface sites ("grafting to" technique).^{4,7–10} Using this method only very small amounts of the polymer (typically less than 5 mg/m²) can be immobilized to the substrates, as once the surface is becoming significantly covered, additional polymer molecules, which are trying to reach the surface, have to diffuse against the concentration gradient built up by the already deposited polymer chains. This leads to a strong kinetic hindrance for the attachment of additional polymer chains to the surface and impedes further film growth. Therefore, the formation of surface-bound polymer monolayers by such a "grafting to" technique is intrinsically limited to low graft densities and low film thicknesses.

A more promising approach for the preparation of covalently attached polymer monolayers is given by the use of immobilized initiators for the *in situ* generation of the grafted polymers. In the systems described in the literature,^{11–14} which follow this approach, mostly grafted azo compounds are used as initiators for the radical chain polymerization of vinyl monomers. In the systems described so far an anchor molecule is immobilized at the surface of the substrate and the initiating species is linked to this anchor molecule in one or several additional reaction steps. However, there are several disadvantages of such a strategy. First, the stepwise generation of the monolayers leads to low graft densities of the surface-attached initiator and consequently polymer, if the surface reactions are not quantitative. Second, incomplete conversions and side reactions cause the formation of structures other than the desired initiator. Such side products are, however, difficult to characterize and even more difficult to quantify as quantitative analysis in organic monolayers is not trivial. This lack of knowledge about the exact composition of the initiator layer has further consequences for the understanding of the mechanism of the subsequent polymerization. It will make a detailed evaluation of reaction steps such as the initiator activation as well as growth and termination of the polymer chains difficult, if not outright impossible. An example

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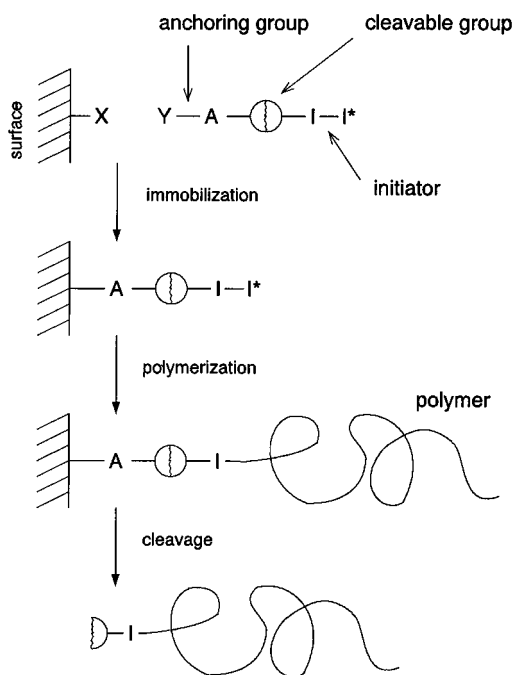


Figure 1. Schematic description of the concept for the preparation of terminally attached polymer monolayers using covalently bonded initiators for radical-chain polymerizations ("grafting from").

for a system in which strong deviations from the idealized structure can be observed is (aminoalkyl)triethoxysilanes, which are frequently used for anchoring molecules to silica surfaces. It has been shown that the silanes in such layers can cross-link to form surface-attached networks and that the amino groups, on the other hand, can have strong interactions with appropriate sites at the surfaces, which both lead to deviations from the simple structural formula expected at first sight. If such a layer is now used for additional surface reactions, the structure of the resulting monolayer will be very difficult to analyze and reproduce.

Finally, in the systems described so far there is no simple way to detach the grafted polymers quantitatively in order to make them available for standard techniques of polymer analysis, e.g., size-exclusion chromatography or light scattering. In the approaches so far the underlying inorganic substrate is dissolved, which becomes increasingly more difficult with increasing thickness of the polymer coating as the substrate becomes less accessible.

In order to avoid these problems we developed a system^{15,16} in which the complete initiator is attached to the substrate's surface in one reaction step. A schematic description of this system is given in Figure 1. It consists of three basic components: an anchoring group (A) linking the initiator to the surface, the initiator itself (I-I), and a cleavable group (C) that allows for the degrafting of the macromolecules after polymerization for analytical purposes. In a first reaction step the initiator is self-assembled on the surface of the substrate. In a subsequent reaction the initiator is activated and polymer is formed *in situ* at the surface of the substrate.

In this paper we report on the formation of poly(styrene) monolayers covalently attached to the surface of high surface area silica gels. The polymer is formed by radical polymerization *in situ* from a self-assembled monolayer of a chlorosilane group containing azo initia-

tor. The azo compound is linked to the surface of the substrate through a base-catalyzed condensation reaction. The synthesis of the azo initiator, the immobilization of the initiator layer onto the surface of the silica, and the principles of the radical-chain polymerization of styrene started from this layer are described.

Experimental Section

Materials. Silica (Aerosil A300, Degussa) with a specific surface area of $285 \pm 15 \text{ m}^2 \text{ g}^{-1}$ according to nitrogen adsorption measurements (BET technique) was dried overnight at $110^\circ\text{C}/10^{-2} \text{ mbar}$. Toluene was distilled under a nitrogen atmosphere from a sodium/potassium alloy using benzophenone as an indicator. Styrene was chromatographically purified over ALOX B, distilled in vacuum from copper(I) chloride, and stored under nitrogen at -30°C . All other solvents and chemicals were used as received.

Characterization. NMR spectra were recorded on a Bruker AC250 spectrometer using CDCl_3 as the solvent. DRIFT spectra were recorded on a Digilab FTS-15/80 at a resolution of 4 cm^{-1} . For transmission FTIR spectroscopy (KBr pellet or film) a Digilab 3240-SPC FTS-40 spectrometer was used. XPS measurements were performed by using a setup from Leybold-Heraeus with monochromatic Mg K α radiation ($E = 1253.6 \text{ eV}$) collecting up to 200 scans. The molar masses were determined by GPC on a Waters 150C using CHCl_3 as the eluent. The equipment was calibrated with narrow molecular weight poly(styrene) standards. DSC traces were recorded on a Perkin-Elmer DSC 2 at a scan rate of 10 K min^{-1} . The decomposition temperatures T_{dec} of the azo compounds are the minima of the exotherms of the DSC traces.

Synthesis of Asymmetric Azo Initiators. A mixture of 100 g (0.86 mol) of neutralized laevulic acid and 50 g (0.86 mol) of acetone was added dropwise to a solution of 112 g (1.72 mol) of KCN and 112 g (0.86 mol) of hydrazine sulfate in 1.5 L of water maintained at 50°C . After complete addition, the solution was stirred for 3 h and then allowed to cool. It was then acidified (pH 4) and cooled to 0°C . At this temperature bromine was added dropwise until it remained in excess and the mixture was stirred for 30 min. The excess of bromine was destroyed with sodium hydrogen sulfite and a white precipitate collected. The filtrate was extracted twice with methylene chloride, and 11 g of **1** could be isolated. The solid was suspended in about 500 mL of 1 N NaOH, stirred for 30 min and filtered. The nonsoluble part (24 g) consisted of the symmetric coupling product 2,2'-azobis(isobutyronitrile) (AIBN). After filtration the solution was acidified, causing the precipitation of 17 g of **1**. The two solid fractions were united and recrystallized from methanol/water (1/5 v/v) (total yield 25 g, 13%). DSC: $T_m = 102^\circ\text{C}$, $T_{\text{dec}} = 120^\circ\text{C}$, $\Delta H_{\text{dec}} = 217 \pm 6 \text{ kJ mol}^{-1}$. IR (KBr): 3600–2500, 2244, 1704 cm^{-1} . ^1H NMR (CDCl_3 in ppm): 9.0–9.5 (b, 1H, CO_2H), 2.2–2.7 (m, 4H, CH_2), 1.71, 1.72, and 1.75 (s, 3H each, CH_3). ^{13}C NMR (CDCl_3 in ppm): 177 (CO_2H), 119 and 117 (CN), 71 and 68 (C_{tert}), 33, 29, 25, and 24 (CH_2 and CH_3). Elem anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$: C, 54.04; H, 6.35; N, 25.14. Found: C, 53.95; H, 6.40; N, 25.14.

To a suspension of 40 g (200 mmol) of phosphorus pentachloride (PCl_5) in 50 mL of methylene chloride cooled with an ice-bath was added dropwise a solution of 10 g (45 mmol) of **1** in 50 mL of methylene chloride. The mixture was allowed to warm to room temperature and stirred overnight. The excess of PCl_5 was filtered off, and the remaining solution was concentrated until no more PCl_5 separated. The mixture was filtered again, and the filtrate was added to 300 mL of cold hexane, causing the separation of **2** as a white solid (9.5 g, 90%). DSC: $T_{\text{dec}} = 120^\circ\text{C}$, $\Delta H_{\text{dec}} = 212 \pm 8 \text{ kJ mol}^{-1}$. IR (KBr): 2992, 2943, 2242, 1740 cm^{-1} . ^1H NMR (CDCl_3 , δ in ppm): 2.9–3.1 (m, 2H, CH_2COCl), 2.4–2.6 (m, 2H, CH_2C), 1.70, 1.72, and 1.75 (s, 3H each, CH_3). ^{13}C NMR (CDCl_3 , δ in ppm): 172 (COCl), 119 and 117 (CN), 71 and 69 (C_{tert}), 41, 32, 25, and 24 (CH_2 and CH_3). Elem anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{ClN}_4\text{O}$: C, 49.90; H, 5.44; Cl, 14.73; N, 23.28. Found: C, 49.85; H, 5.33; Cl, 14.58; N, 23.30.

To a solution of 40 mmol of the respective alcohol and 6.5 mL (80 mmol) of pyridine in 50 mL of methylene chloride at 0 °C was added dropwise a solution of 8 g (33 mmol) of **2** in 50 mL of methylene chloride. The mixture was allowed to warm to room temperature and stirred overnight. Then the solution was washed twice with 2 N H₂SO₄, aqueous NaHCO₃, and water. The organic layer was dried over Na₂SO₄, and the solvent was evaporated. The resulting pale yellow oil was dissolved in a small amount of methylene chloride and poured into 300 mL of cold hexane. Thus, the respective ester **3** or **4** separated as a white solid (90% yield).

Allylic ester 3. DSC: $T_{\text{dec}} = 122\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 236 \pm 5\text{ kJ mol}^{-1}$. IR (KBr): 3089, 2992, 2943, 2244, 1738 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 5.8–5.9 (m, 1H, =CH–), 5.2–5.4 (m, 2H, CH₂=), 4.6 (d, 2H, CH₂O), 2.3–2.5 (m, 4H, CH₂CH₂) 1.68, 1.70, and 1.72 (s, 3H each, CH₃). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 131 (=CH–) 118 (CH₂=), 119 and 117 (CN), 71 and 66 (C_{tert}), 65 (CH₂O), 33, 29, 25, and 24 (CH₂ and CH₃). Elem anal. Calcd for C₁₃H₁₈N₄O₂: C, 59.53; H, 6.92; N, 21.36. Found: C, 59.45; H, 6.95; N, 21.50.

Undecenylic Ester 4. DSC: $T_{\text{dec}} = 121\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 247 \pm 8\text{ kJ mol}^{-1}$. IR (KBr): 3077, 2989, 2928, 2856, 2244, 1737 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 5.8–5.9 (m, 1H, =CH–), 5.2–5.4 (m, 2H, CH₂=), 4.6 (d, 2H, CH₂O), 2.3–2.5 (q, 2H, COCH₂CH₂), 2.0–2.1 (q, 2H, COCH₂CH₂CH₂), 1.72, 1.74, and 1.75 (s, 3H each, CH₃), 1.2–1.6 (b, 10H, CH₂). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 139 (=CH–) 114 (CH₂=), 119 and 118 (CN), 71 and 68 (C_{tert}), 65 (CH₂O), 34, 33, 28–29 (4 peaks), 25–26 (3 peaks), and 24 (CH₂ and CH₃). Elem anal. Calcd for C₂₁H₃₄N₄O₂: C, 67.35; H, 9.15; N, 14.96. Found: C, 67.26; H, 9.00; N, 14.92.

Hydrosilation Reactions. To a suspension of 3 g of the respective ester **3** or **4** in 30 mL of the respective chlorosilane was added a solution of 30 mg of hexachloroplatinic acid in 0.5 mL of dimethyl ether/ethanol (1/1 v/v), and the mixture was heated to reflux for 3 h. After that time all of the solid dissolved, indicating the completion of the reaction. The excess of the silane was recovered by distillation, and the product was dried in vacuo, yielding pale green oils in quantitative yields. Residual platinum catalyst was removed by filtration of a CH₂Cl₂ solution of the product over anhydrous sodium sulfate.

Azomono-chlorosilane (AMCS) 5. DSC: $T_{\text{dec}} = 121\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 180 \pm 7\text{ kJ mol}^{-1}$. IR (film): 2990, 2960, 2942, 2899, 2244, 1737, 1257, 1181 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 4.1 (t, 2H, OCH₂), 2.4–2.5 (m, 6H, CH₂), 1.71–1.73 (3 s, 3H each, CCH₃), 0.8 (m, 2H, SiCH₂), 0.4 (s, 6H, SiCH₃). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 117 and 118 (CN), 70 and 71 (C_{tert}), 67 (CH₂O) 33, 30, 29, 25, 23, 22 (CH₂ and CH₃), 15 (SiCH₂), 2 (SiCH₃). Elem anal. Calcd for C₁₅H₂₅ClN₄O₂Si: C, 50.48; H, 7.06; Cl, 9.93; N, 15.70; Si, 7.87. Found: C, 50.47; H, 7.02; Cl, 9.75; N, 15.60; Si, 7.96%.

Azodichlorosilane (ADCS) 6. DSC: $T_{\text{dec}} = 121\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 181 \pm 8\text{ kJ mol}^{-1}$. IR (film): 2991, 2943, 2890, 2244, 1737, 1181 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 4.1 (t, 2H, OCH₂), 2.4–2.5 (m, 6H, CH₂), 1.71–1.73 (3 s, 3H each, CCH₃), 0.8 (m, 2H, SiCH₂), 0.4 (s, 3H, SiCH₂). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 117 and 118 (CN), 68 and 71 (C_{tert}), 68 (CH₂O), 33, 29, 25, 24, 22, 21 (CH₂ and CH₃). Elem anal. Calcd for C₁₄H₂₂Cl₂N₄O₂Si: C, 44.56; H, 5.88; Cl, 18.79; N, 14.85; Si, 7.44. Found: C, 44.53; H, 5.85; Cl, 18.78; N, 14.97; Si, 7.47.

Azotrichlorosilane (ATCS) 7. DSC: $T_{\text{dec}} = 121\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 176 \pm 9\text{ kJ mol}^{-1}$. IR (film): 2991, 2943, 2898, 2245, 1738, 1178 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 4.1 (t, 2H, OCH₂), 2.4–2.6 (m, 4H, CH₂CO), 1.9 (m, 2H, OCH₂CH₂), 1.71–1.73 (3 s, 3H each, CCH₃), 0.8 (m, 2H, SiCH₃). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 117 and 118 (CN), 68 and 71 (C_{tert}), 68 (CH₂O), 33, 29, 25, 24, 22, 21 (CH₂ and CH₂).

Azoundecylmonochloro silane (AUMCS) 8. DSC: $T_{\text{dec}} = 121\text{ }^{\circ}\text{C}$, $\Delta H_{\text{dec}} = 201 \pm 8\text{ kJ mol}^{-1}$. IR (film): 2290, 2960, 2942, 2899, 2244, 1737, 1257, 1181 cm⁻¹. ¹H NMR (CDCl₃, δ in ppm): 4.1 (t, 2H, OCH₂), 2.4–2.5 (m, 6H, CH₂), 1.71–1.73 (3 s, 3H each, CCH₃), 1.1–1.4 (b, 18H, CH₂), 0.8 (m, 2H, SiCH₂), 0.4 (s, 6H, SiCH₃). ¹³C NMR (CDCl₃, δ in ppm): 171 (CO), 117 and 118 (CN), 68 and 71 (C_{tert}), 66 (CH₂O), 34, 33,

Table 1. Maximum Graft and Area Densities of the Various Azosilanes on Silica Aerosil A300 As Determined by DSC

initiator	graft density δ [$\mu\text{mol g}^{-1}$]	area density Γ [$\mu\text{mol m}^{-2}$]
SiO ₂ –AMCS (9)	525	1.84
SiO ₂ –ADCS (10)	680	2.39
SiO ₂ –ATCS (11)	760	2.67
SiO ₂ –AUMCS (12)	520	1.82

31–29, 25, 23, 22 (CH₂ and CH₃), 15 (SiCH₂), 2 (SiCH₃). Elem anal. Calcd for C₂₃H₄₁ClN₄O₂Si: C, 58.88; H, 8.81; Cl, 7.56; N, 11.94; Si, 5.99. Found: C, 58.77; H, 9.01; Cl, 7.47; N, 11.87; Si, 5.92.

Immobilization of the Chlorosilanes to Silica Gel.

Under an atmosphere of dry nitrogen a solution of 1.5 g of the respective azochlorosilanes 5–8 in 50 mL of toluene was added to a suspension of 3 g of silica gel in 100 mL of toluene. A total of 3 mL of pyridine was added, and the mixture was stirred for 12 h. The modified silica gels were centrifuged and washed with toluene, ethanol, acidified (HCl) ethanol/water (1/1 v/v, pH 3), ethanol/water (1/1 v/v), ethanol, and diethyl ether. The remaining white solids were dried overnight at 10⁻² mbar. The graft densities δ (in mol g⁻¹) of the azosilanes can be determined from elemental analysis according to eq 1 from the carbon, nitrogen, or hydrogen content or according to eq 2 from the SiO₂ residue remaining after combustion. g_E are the

$$\delta = g_E/M_E Z \quad (1)$$

$$\delta = \frac{1 - g(\text{SiO}_2)}{M_F} \quad (2)$$

respective element (C, H, or N) contents and $g(\text{SiO}_2)$ is the SiO₂ content of the sample, M_E and M_F are the element or molecule fragment (azosilane without Cl) masses, and Z is the number of the elements in the immobilized molecule fragment.

A second possibility to calculate δ is to use the integral of the decomposition exotherm I_{dec} in the DSC trace of the immobilized initiator and the molar enthalpy of decomposition ΔH_{dec} of the respective chlorosilane:

$$\delta = \Delta H_{\text{dec}}/I_{\text{dec}} \quad (3)$$

SiO₂–AMCS 9. IR (DRIFT): 3740–3000, 2990, 2960, 2942, 2899, 2244, 1737 cm⁻¹. DSC: $T_{\text{dec}} = 123\text{ }^{\circ}\text{C}$, $I_{\text{dec}} = 96 \pm 2\text{ J g}^{-1}$ (averaged value from five measurements), $\delta_{\text{DSC}}(\text{AMCS}) = 533 \pm 8\text{ } \mu\text{mol g}^{-1}$ (elem anal. C, 9.46; N, 2.83; residue (SiO₂), 83.26), $\delta_C(\text{AMCS}) = 525 \pm 16\text{ } \mu\text{mol g}^{-1}$, $\delta_N(\text{AMCS}) = 503 \pm 53\text{ } \mu\text{mol g}^{-1}$, $\delta_{\text{SiO}_2}(\text{AMCS}) = 521 \pm 31\text{ } \mu\text{mol g}^{-1}$.

SiO₂–ADCS 10. IR (DRIFT): 3740–3000, 2991, 2962, 2945, 2897, 2244, 1736 cm⁻¹. DSC: $T_{\text{dec}} = 123\text{ }^{\circ}\text{C}$; $I_{\text{dec}} = 123 \pm 4\text{ J g}^{-1}$ (averaged value from five measurements), $\delta_{\text{DSC}}(\text{ADCS}) = 680 \pm 6\text{ } \mu\text{mol g}^{-1}$.

SiO₂–ATCS 11. IR (DRIFT): 3740–3000, 2993, 2965, 2947, 2899, 2246, 1737 cm⁻¹. DSC: $T_{\text{dec}} = 123\text{ }^{\circ}\text{C}$; $I_{\text{dec}} = 134 \pm 5\text{ J g}^{-1}$ (averaged value from five measurements), $\delta_{\text{DSC}}(\text{ATCS}) = 760 \pm 8\text{ } \mu\text{mol g}^{-1}$.

SiO₂–AUMCS 12. IR (DRIFT): 3740–3000, 2991, 2959, 2943, 2899, 2247, 1735 cm⁻¹. DSC: $T_{\text{dec}} = 123\text{ }^{\circ}\text{C}$; $I_{\text{dec}} = 104 \pm 4\text{ J g}^{-1}$ (averaged value from five measurements), $\delta_{\text{DSC}}(\text{AUMCS}) = 520 \pm 7\text{ } \mu\text{mol g}^{-1}$.

The graft density of the azomono-chlorosilane AMCS was varied by following the described procedure but changing the AMCS/silica ratio during immobilization (Table 1). The graft densities of the resulting materials were determined by analyzing the DSC traces according to eq 3.

Formation of Polymer Monolayers. Under an atmosphere of dry nitrogen 1.8 g of SiO₂–AMCS was suspended in 300 mL of styrene/toluene (1/2 v/v), degassed in vacuum through repeated freeze–thaw cycles, and heated to 60.0 \pm 0.1 °C in a thermostat. After chosen periods of time (1.5–14 h) samples (20 mL) were withdrawn under nitrogen and placed in a centrifuge tube (50 mL). The tubes were filled up with

toluene and then centrifuged at 8000 min^{-1} for at least 30 min. The supernatant solution, which contained the nonattached polymer was decanted, poured into excess methanol (at least 10 times the volume of the toluene solution), and filtered off. The solid remaining after decanting was then further extracted with toluene as described until no more precipitate formed when the supernatant liquid was added dropwise to methanol. Depending on the graft density of the material and the total amount of polymer, 5–10 cycles of this procedure were necessary to remove the nonbonded polymer. Both the grafted **13** and the nonbonded polymer were freeze-dried from benzene. The molecular weight of the nonbonded polymer was determined by GPC. In order to get the same information about the grafted material **13**, the polymer was cleaved off from the surface of the substrate.

Degrafting Procedure. A total of 500 mg of the polymer-modified silica gel **13** was suspended in 100 mL of toluene. A total of 10 mL MeOH and 50 mg of *p*-TsOH were added, and the mixture was heated to reflux overnight. The products were isolated by the same extraction procedures as described above for the nonbonded polymer. Using this method about 90–98% of the organic material can be cleaved off according to combustion analysis of the residual SiO_2 . This yield was found to be independent of the original graft density of the SiO_2 -PS material studied. After freeze-drying of the degrafted polymers, the molecular weights were determined by GPC measurements.

Results and Discussion

One of the basic requirements for the synthesis of controlled polymer monolayers by polymerization started from surface-attached initiator molecules is the control of the chemical composition and graft density of the initiators. As reactions in surface-attached monolayers are not easily quantified, it is desirable to achieve the immobilization of the initiator in a one-step procedure. Additionally, the surface reaction has to be self-limiting otherwise uncontrolled multilayer formation will occur. To obtain a high graft density, it is desirable that the reactivity of the initiator molecule is high under the given reaction conditions.

The synthesis of the initiator used in this study is shown in Figure 2. It consists of an azo group which is structurally similar to AIBN and a monofunctional chloro silane head group, which connects the initiator to the surface of the substrate. The ester group connecting the initiating group and the anchor can act as a "break-seal" group. Hence, this ester can be cleaved after completion of the layer formation, and the polymer can be removed from the surface and analyzed.

Synthesis of Asymmetric Azo Compounds with a Chlorosilane Head Group. Although the synthesis of aliphatic azo compounds with functional groups has been well-established,¹⁷ not many examples are known for the preparation of asymmetric aliphatic azo compounds. Therefore, the key step for the synthesis of the azochlorosilanes is the formation of the azomonocarboxylic acid (**1**) as described in Figure 2. For this purpose the method of Haines and Waters,¹⁸ who described the preparation of the symmetric analogue 4,4'-azobis(4-cyanovaleric acid), was modified using an equimolar mixture of neutralized laevulic acid and acetone as oxo compounds, yielding directly the desired azo compound **1**. Two products can be isolated in significant amounts: AIBN (ca. 15% yield) and the desired azomonocarboxylic acid (**1**; 10–20%). Although the yield is only moderate due to several side reactions, the described procedure was found to be quite advantageous as the desired carboxylic acid can easily be separated from all

other compounds due to great differences in polarity and solubility.

The preparation of the acid chloride **2** was achieved by reacting **1** with an excess amount of PCl_5 in methylene chloride as described in the literature for the symmetrical compound.¹² Great care must be taken to remove all remaining PCl_5 from the product, as it was found to be to some extent soluble in methylene chloride. However, acid chloride and PCl_5 can be separated by careful partial evaporation of the solvent and filtration of the reaction mixture until no more pale yellow solid (PCl_5) separates. The acid chloride **2** is then isolated by pouring the remaining CH_2Cl_2 solution into cold hexane, causing the separation of **2** as a white powder (75–80%). The allylic or undecenyl esters **3** and **4** were synthesized from **2** and the respective unsaturated alcohol in the presence of equimolar amounts of pyridine in yields of 70–90% in each case.

It is known that allylic esters can be readily hydrosilylated with chlorosilanes using a variety of different platinum catalysts.^{19,20} However, all methods described were performed at high temperatures (mostly of about 100°C). Such conditions are not suitable for the preparation of azo compounds as they would decompose within a few minutes at such high temperatures. At room temperature, however, long induction periods (several hours), where apparently no reaction takes place, were observed, followed by a very rapid exothermic reaction with a strong increase of the temperature. Similar observations have been frequently made during other hydrosilylation reactions.^{19,20} However, no such delay is observed if the hydrosilylations are performed by refluxing the reaction mixtures in excess chlorosilane. Due to the low boiling points of the chlorosilanes, no decomposition of the azo compounds occurs during the reaction. From NMR analysis it can be concluded that the resulting azochlorosilanes **5–8** consist exclusively of the anti-Markovnikov addition products.

Immobilization of the Azo Initiators. The azochlorosilanes **5–8** were immobilized onto silica gel under inert conditions in the presence of pyridine or triethylamine, yielding the SiO_2 derivatives **9–12**. The silica gels were dried before use at 120°C and 10^{-2} mbar for at least 12 h. This procedure is probably not sufficient enough to remove all the water adsorbed at the SiO_2 surface. However, it should be noted that monofunctional silanes can only form disiloxanes upon hydrolysis, which cannot react with the surface and are washed away during workup. Thus, the problem of di- or trifunctional compounds that strongly differing graft densities are obtained if the amount of residual water changes is avoided, and reproducible graft densities can be achieved.

The influence of the base on the immobilization reaction was studied in a control experiment, where octadecyldimethylchlorosilane (ODMCS) and silica gel were reacted under identical conditions with and without the addition of a tertiary amine. According to elemental analysis, about 4 times more of the silane can be immobilized if the base is added to the reaction mixture. The base acts as an acid scavenger and additionally could catalyze the surface reaction by deprotonation of the surface groups, thus facilitating the nucleophilic substitution during the condensation reaction.^{21–23}

Figure 3 shows the IR spectra of unmodified silica gel (a) and of immobilized AMCS **5** (b). The absorption

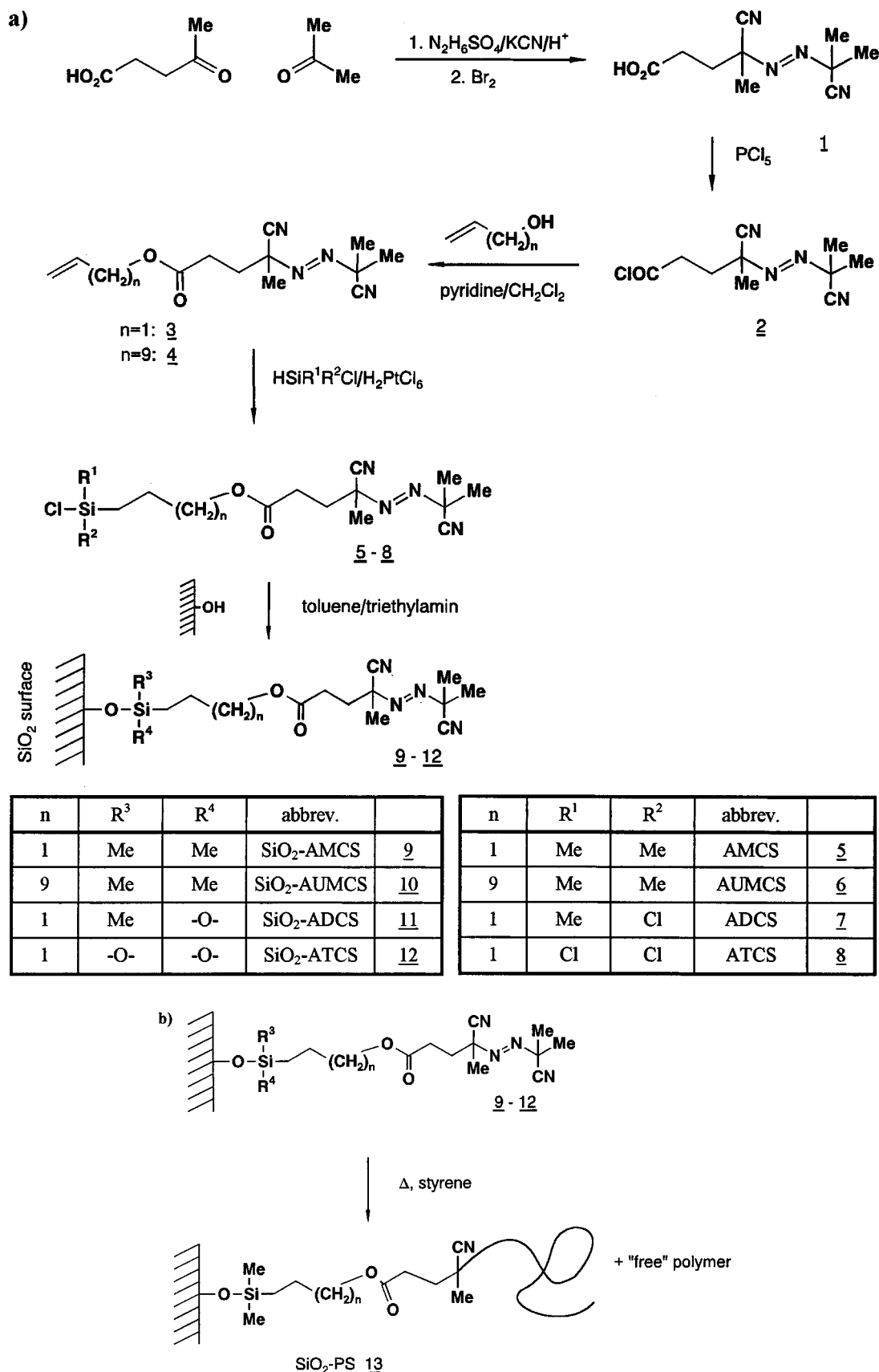


Figure 2. (a) Synthesis of self-assembled monolayers of azo initiators. (b) Preparation of molecularly thin polymer layers attached to a silica surface.

bands due to the carbonyl (1740 cm^{-1}) and nitrile bonds (2244 cm^{-1}) and the C–H stretching vibrations ($2800\text{--}2990\text{ cm}^{-1}$) of the initiator molecule are clearly visible. The sharp vibration band at 3750 cm^{-1} in the spectrum

of the bare substrate which is often attributed to the stretching vibration of the SiOH groups²⁴ disappears after the silane treatment. In the spectrum of SiO₂–AMCS a broad band between 3700 and 3000 cm^{-1} is

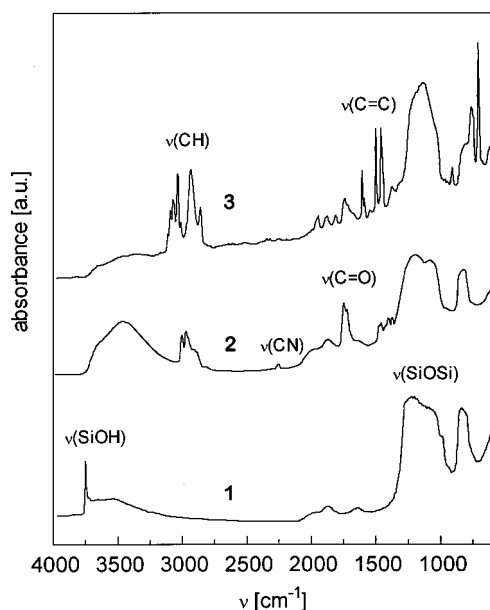


Figure 3. DRIFT spectra of (a) unmodified silica gel, (b) silica gel with immobilized azo initiator (SiO_2 -AMCS (**9**)) and (c) immobilized poly(styrene) (**13**) generated via radical graft polymerization using SiO_2 -AMCS (**9**) as the initiator.

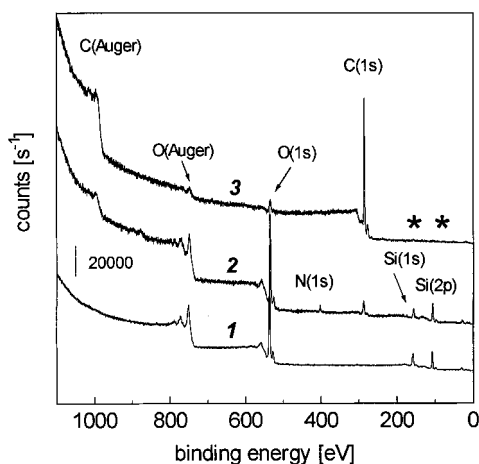


Figure 4. XP spectra of (a) unmodified silica gel, (b) SiO_2 -AMCS (**9**) and (c) SiO_2 -PS (**13**) generated using **9** as the initiator.

observed which is caused by water that is absorbed during the aqueous workup.

The XP spectra of the unmodified substrate and of the silane-treated silica gel (SiO_2 -AMCS) are depicted in Figure 4. The spectrum of the SiO_2 substrate only shows signals due to the presence of silicon (152 eV, $\text{Si}(2s)$; 100 eV, $\text{Si}(2p)$) and oxygen atoms (533 eV, $\text{O}(1s)$). This observation is in good agreement with the results of elemental analysis of the bare substrate, where only traces of carbon ($<0.3\%$) were found. After immobilization of the azo initiator **5**, two new signals appear in the survey spectrum of **9**, due to the carbon (287 eV, $\text{C}(1s)$) and nitrogen atoms (402 eV, $\text{N}(1s)$) of the azo compound. The results of a detailed analysis²⁵ of these signals are in good agreement with the chemical composition of the initiator molecules.

The simplest way to quantify the amount of immobilized silane is to investigate the material by elemental analysis. A second possibility for the measurement of the graft density is to follow the thermal decomposition of the attached azo molecules by DSC,

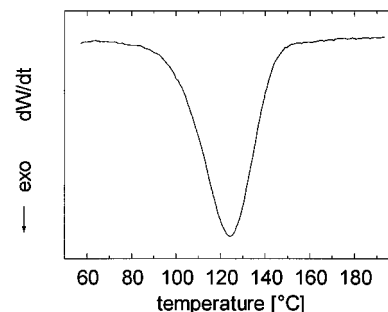


Figure 5. DSC trace of SiO_2 -AMCS (**9**). Heating rate 10 K min^{-1} .

as this is a strongly exothermic process (Figure 5). If it is assumed that the thermal behavior of the azo compounds is not strongly affected by their binding to the surface, the graft density can be evaluated by monitoring the signal of the exothermic decomposition in the DSC traces of the azo-modified SiO_2 samples. This assumption seems to be reasonable as both the pure azo compounds and SiO_2 derivatives show identical minima in the DSC trace (ca. 120°C). Based on the molar enthalpy of decomposition ΔH_d of the chlorosilane ($180 \pm 7 \text{ kJ mol}^{-1}$), its graft density can be calculated from the integral of the DSC signal according to eq 3. The results of graft density measurements by elemental analysis were found to be in good agreement with the values obtained from DSC measurements. Furthermore, the decomposition temperatures and enthalpies of decomposition of the immobilized compounds are in good agreement with values obtained for AIBN not in contact with a surface.²⁶

The graft densities of the immobilized azochlorosilanes as determined by DSC are summarized in Table 1. The area density Γ of the silanes was calculated from the graft density δ and the specific surface area of the bare substrate ($285 \pm 5 \text{ m}^2/\text{g}$). From these values it can be derived that about $0.8\text{--}1.6$ initiator molecules/ nm^2 are immobilized or that the averaged distance between two anchoring sites is $0.8\text{--}1.0 \text{ nm}$. There has been considerable argument in the literature²⁴ about the absolute number of silanol groups on a silica gel. The values range (depending on the nature of the SiO_2 and the method of determination) between 0 and 18 groups/ nm^2 , with most recent references agreeing on $4\text{--}5 \text{ SiOH}/\text{nm}^2$. We believe, however, that this value is not relevant for the work described here, as for geometric reasons not all of those groups can react with the chlorosilane and the number of silane groups immobilized to the surface is only limited by the steric demands of the dimethylchlorosilyl head group.²⁷ The graft density of the azo initiator is therefore in good agreement with the graft density of dimethylalkylchlorosilanes with chain lengths between 2 and 18 carbon atoms if all compounds are immobilized using the same reaction conditions. That the amount of immobilized azo compound does not depend strongly on the size of the molecule is also supported by the observation that the azosilanes AMCS (**5**) and AUMCS (**6**) yield comparable graft densities despite the fact that the spacers which decouple the azo moiety from the surface have very different chain lengths (C_3 vs C_{11}).

As shown in Table 1, higher graft densities can be achieved using self-assembled monolayers of the di- and trifunctional chlorosilanes **7** and **8** as polymerization initiators. It is known^{28–31} that these compounds can

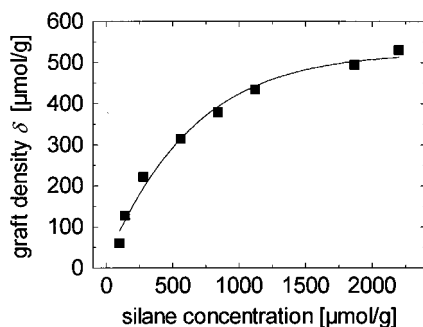


Figure 6. Graft densities of SiO_2 -AMCS (**9**) as a function of the silane concentration employed for immobilization. The silane concentration is given in the same unit as the graft density to allow for comparison.

react with each other prior to the reactions with the surface if small amounts of water can be present in the reaction mixture (e.g., moisture absorbed on the substrate or dissolved in the solvent). This leads to cross-linked and disordered silane multilayers^{28–31} as not all azo molecules need to be directly bonded to the surface but some of them are only connected to the substrate via a link to other immobilized molecules (not shown in the structure formula in Figure 2). As the amount of moisture remaining in the reaction mixture is not easily controlled, the graft densities of these silanes are often changing considerably from run to run. Therefore, structurally well-defined monolayers of the azo molecules can only be obtained in a reproducible way by using the monochlorosilanes AMCS (**5**) and AUMCS (**6**). The structural differences between the mono-, di-, and trifunctional silane can be seen in ^{29}Si solid-state NMR (CP-MAS technique) measurements. The results of these measurements will be published elsewhere.^{32,33}

In order to study the influence of the surface concentration of the initiator on the polymerization process, it is necessary to control the graft density of the azo compound. Thus, several silanization experiments were performed, in which the starting silane/silica ratio was systematically varied. In Figure 6 the graft density of the obtained SiO_2 -AMCS samples is shown as a function of the silane concentration. It can be seen that the surface initiator concentration can be controlled between complete coverage, i.e., all silanol groups which are accessible for geometric reasons²⁷ have reacted (about $550 \mu\text{mol/g} = 1.9 \mu\text{mol/m}^2$), and the detection limit of the DSC experiment (ca. $50 \mu\text{mol/g} = 0.2 \mu\text{mol/m}^2$). This simple way to control the graft density of the initiator clearly demonstrates the advantage of using a one-step procedure and a monofunctional anchoring group.

Surface Polymerizations. The polymerization reactions of styrene with the surface-attached initiators were performed in toluene solutions at 60°C . Samples were withdrawn after selected periods of time. As the initiator is bound to the surface only by one end and the second part of the initiator can diffuse into solution and start a polymerization reaction there, not all polymer which had formed is covalently attached to the substrate. An additional amount of nonbonded polymer may result from transfer reactions of a grafted growing chain to solvent or monomer molecules or thermal polymerization in solution without initiator. Therefore, the polymer-modified silica gels were carefully extracted several times with toluene and centrifuged, until no precipitate formed when the supernatant solution was added dropwise to an excess of methanol. In most cases

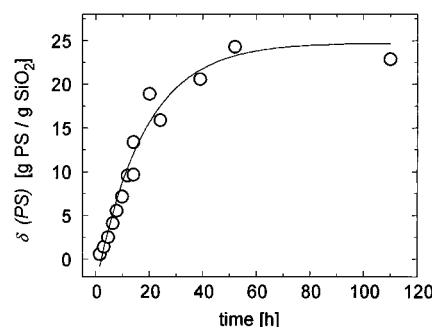


Figure 7. Graft density of surface-attached poly(styrene) chains (SiO_2 -PS (**13**)) as a function of polymerization time.

about 5–10 cycles were enough to remove all nonbonded poly(styrene) from the desired product. Control experiments with mixtures of silica gel and poly(styrene) demonstrated that polymer simply adsorbed to the silica surface can be readily separated by extracting the material as described above. However, all polymer could be extracted after treatment of the material with MeOH in toluene using *p*-TsOH as a catalyst. This transesterification reaction leads to a cleavage of the ester group connecting the polymer to the surface. The complete removal after cleavage demonstrates clearly that the polymer had been indeed covalently attached to the surface. A more detailed discussion of the degrafting reaction will follow further below.

At first the polymer-silica composites were characterized qualitatively. A typical FTIR spectrum of the poly(styrene)-modified silica gels is depicted in Figure 3 (trace c) and appears as the superposition of the spectra of the two components silica gel and poly(styrene). Due to the high graft density of the polymer (see below) in comparison to that of the initiator, no signals of the azo compound or its decomposition products can be seen.

The polymer-modified silica gels were also investigated by XP spectroscopy. A comparison of the XP spectra of the initiator monolayer (Figure 4, trace b) and the covalently bonded poly(styrene) (Figure 4, trace c) shows a strong enhancement of the carbon signal at 287 eV (C(1s)). A second small signal in this region is found at about 292 eV. This so-called "shake-up satellite" is caused by the π, π^* -transition of the phenyl rings of poly(styrene).³⁴ Both signals can be fitted according to literature values for the XPS analysis of bulk poly(styrene).^{25,34} Additionally, in the spectrum of the polymer-modified silica gel the signals of the underlying substrate (Si(1s), Si(2p), and O(1s)) are strongly attenuated or cannot be detected any longer (depending on the graft density of the polymer). This can serve as an indication that the polymer films around the silica particles are homogeneous and thicker than the escape depth of the photoelectrons generated by the X-ray irradiation.³⁵ These observations agree well with the results of transmission electron microscopy measurements³⁶ on the polymer-modified silica gels.

In order to obtain quantitative information about the graft densities of the covalently attached polymer layers, the material was investigated by elemental analysis. Figure 7 shows the graft densities of the SiO_2 -PS samples withdrawn after different times of polymerization at 60°C . As can be seen from this plot the amount of polymeric material immobilized to the substrate increases steadily during the first 20 h of polymerization. Until then, a material is formed that shows

a graft density of about 20 g of poly(styrene)/1 g of SiO₂. This result is in good agreement with the kinetics of the decomposition of the immobilized azo compound as at that time not even half of the initiator is decomposed. Indeed, the graft density further increases with increasing reaction time. After about 30 h, which is approximately 1.5 half-life times of the initiator, a material is obtained which consists of about 96 wt % poly(styrene). This value corresponds to a graft density of ca. 25 g of PS/g of SiO₂.

To prove that the polymerization reaction has indeed started from the immobilized azo molecules, a dispersion of the SiO₂-AMS was refluxed in toluene for 11 h, thus completely deactivating the azo initiator. The obtained material was then used in a polymerization procedure as described above. As expected, only a very small amount of polymer could be attached to the surfaces. From elemental analysis a graft density of $\delta = 0.07$ g of PS/g of SiO₂ was calculated after subtraction of the material content due to the decomposed azo compound (obtained from elemental analysis of some part of the material prior to polymerization). The graft density of the attached material is thus about 2 orders of magnitude lower than that of SiO₂ material prepared from a nondeactivated azo-modified silica as described above.

The at first surprising observation that some polymer at all was attached to the surface despite the fact that all initiator was deactivated can be explained by a closer analysis of the products of the azo decomposition. It is known that thermally decomposed azo compounds with a structure similar to AIBN consist of a variety of products, some of them containing a ketenimin or a methacrylnitrile group.¹⁷ Suter and co-workers³⁷ have shown in a series of experiments that such surface-attached compounds can act as (co)monomers during the thermally induced polymerization of styrene (in solution), thus resulting in some surface-attached polymer chains. The surface attachment is therefore caused by a completely different mechanism compared to the polymerization induced by radicals directly attached to surfaces. Indeed, the results of the experiments described here with azo compounds decomposed prior to polymerization are in good quantitative agreement with the experiments, where surface polymerizable groups were incorporated into growing PS chains.³⁷

An essential requirement for the understanding of the polymerization mechanism is the possibility to cleave off the polymer after completion of the layer formation. To achieve this, it is important that groups which can be cleaved are readily accessible. For example, treatment of the silica gel with hydrofluoric acid, which has been used to remove polymer attached to a surface through dissolution of the substrate,¹² was found to be unsuccessful in the case of the materials prepared by the technique described here. Even after treatment for many days still particles consisting of silica and polymer remained. The reason for this could be that the SiO₂ core is shielded from the HF solution by the thick, hydrophobic polymer layer.

Quantitative separation of the polymer, however, can be achieved if the cleavage reaction is carried out in a good solvent for the polymer. Transesterification reactions carried out with methanol/*p*-toluenesulfonic acid (Figure 8) were successful if sufficiently large amounts of toluene were used as a cosolvent, so that the reaction solution was a good solvent for the polymer (toluene contents > 85%). According to elemental analysis

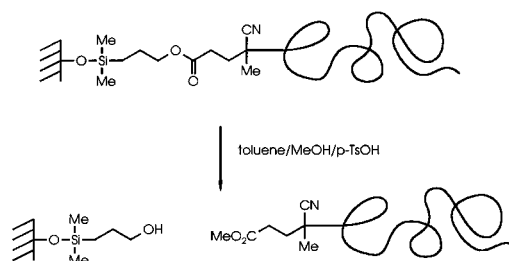


Figure 8. Degrafting of the surface-attached polymer by transesterification.

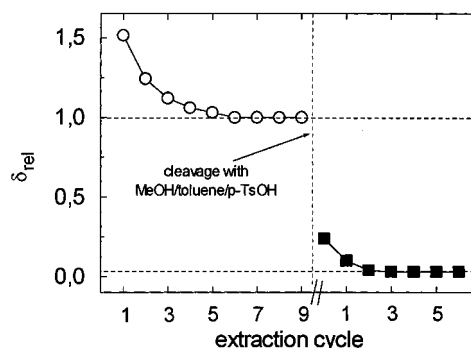


Figure 9. Removal of polymer from the reaction medium during solvent extraction of the polymer-modified silica. After 9 extraction cycles, a degrafting procedure as shown in Figure 8a was performed. Experimental details are given in the text.

almost all organic material could be removed by this procedure (Figure 9) independent of the graft density of the starting material. Whereas the graft density of the polymer remained constant even when many extraction steps with a good solvent, i.e., toluene, for the polymer were performed (the initial loss in the first extraction cycles seen in Figure 9 is caused by removal of physically adsorbed and/or entangled polymer from the as-obtained reaction solution), only a small portion of the organic components (final graft density about 0.05 g/g of silica) remained attached to the surface of the silica gel after degrafting (Figure 9). The residual organic material, which is still on the silica gel after cleaving off of the polymer, is due to the alcohol component which is left at the surface after transesterification (Figure 8). The amount of residual organic material agrees very well with the value calculated if the known graft density of the initiator (550 μ mol/g) and the molecular weight of the fragment still attached to the surface are taken.

After cleavage of the ester group the molecular weight of the polymer can be determined by size-exclusion chromatography and light scattering. A typical GPC trace of the obtained polymer is depicted in Figure 10. It can be seen that the polymer which had been attached to the surface consists of high molecular weight material. The dependence of the molecular weight of the terminally attached polymer molecules on the reaction conditions will be described in an upcoming paper.

For the calculation of the molecular weight of the polymer from the GPC trace with the help of a calibration curve, it is important to know whether the polymer has indeed a linear structure, as implied in Figure 2, or whether strong branching in the polymer occurs. It could be argued that the confinement of the growing chains to a molecularly thin surface layer could increase the possibility for transfer to already formed polymer attached to the surface, thus leading to stronger branch-

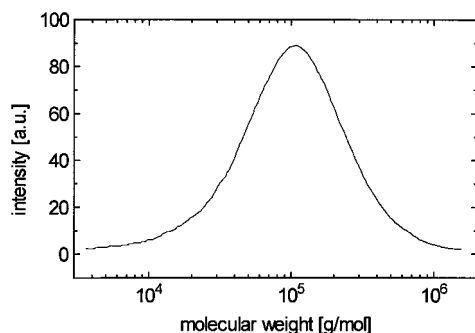


Figure 10. GPC trace of a tethered poly(styrene) isolated after degrafting by transesterification. Polymerization conditions: $T = 60\text{ }^{\circ}\text{C}$; $t = 6\text{ h}$; initiator = $\text{SiO}_2\text{-AMS}$ (9).

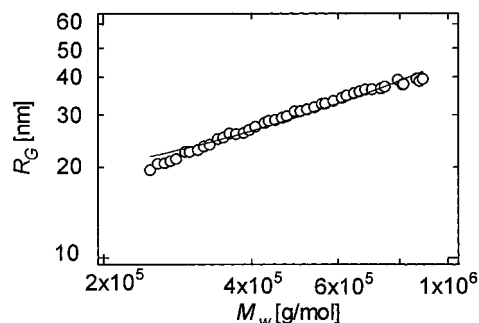


Figure 11. Radius of gyration R_g vs molecular weight of a degrafted polymer according to GPC–light scattering coupling measurements.

ing. Excessive branching has indeed been observed in one system, described in a paper by Revillon et al., who studied the surface polymerization of vinylbenzyl chloride.¹³ However, this result may not be applicable to other systems as vinylbenzyl chloride is known to have a high transfer constant to the polymer and also in a solution polymerization of this particular monomer branching does occur. Excessive branching would result in a more globular structure of the polymer and consequently in a wrong value (underestimation) of the molecular weight obtained from the GPC measurements. Such a difference in the structure of the polymer can be directly seen if the relation between the radius of gyration and the molecular weight of the degrafted chains is investigated. This relation can be obtained from measurements with a GPC/light scattering coupling, in which the polymers are separated according to size in the GPC columns and static light scattering measurements are performed on the eluent.^{38,39} From these measurements the radius of gyration R_g and the molecular mass for all different fractions are calculated. A plot of R_g vs the logarithm of the molecular weight M_w for a typical sample is shown in Figure 11. The slope of the straight line (0.59) is very comparable to that of other polymers (also 0.59)^{38,39} obtained by radical-chain polymerization, and thus excessive branching in the materials can be excluded.

Conclusions

Self-assembled monolayers of radical-chain initiators attached to the surfaces of a high surface area silica gel can be used for the preparation of monolayers consisting of terminally attached polymer chains. Especially, azo compounds with a monofunctional chlorosilane head group proved to be suitable for the preparation of initiator monolayers with reproducible high graft densi-

ties. When this azo-modified silica gel is used for the radical-chain polymerization of styrene, high molecular weight polymer is formed and molecularly thin polymer layers with a high graft density of the attached material are obtained. It could be shown that, despite the confinement of both growing active centers and the polymer molecules formed during the process to a very small reaction zone at the surface of the particles, no cross-linking or excessive branching of the terminally attached chains does occur. The graft density of the polymer can be adjusted in a wide range simply by controlling the conversion of the initiator. A detailed study of the mechanism and the kinetics of this type of polymerization will be given in subsequent publications.

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