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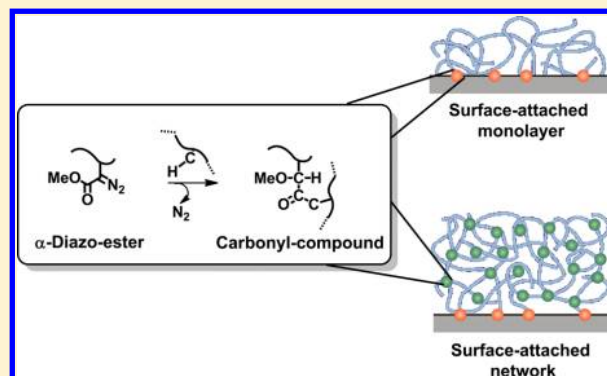
Preparation of Surface-Attached Polymer Layers by Thermal or Photochemical Activation of α -Diazoester Moieties

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ABSTRACT: We report on the attachment of polymer monolayers or surface-attached, polymer networks onto SiO₂ and/or polymer surfaces using thermo- and photoreactive α -diazoester groups. In the prior case, the α -diazoester groups are introduced into the system in the form of self-assembled monolayers of appropriately functionalized silanes. The monolayer decorated substrates are coated by polymer films and the α -diazoester groups in the monolayer are activated by heat or irradiation with UV-light. Upon activation, they cleave off nitrogen and the resulting carbene intermediates insert into C–H bonds of neighboring polymer chains. As a result of this binding process, surface-attached monolayers of the deposited polymer are obtained. When the polymers themselves carry such reactive moieties, the photo- or thermal activation leads to cross-linking of the polymers and thin surface-attached polymer networks result from the same process. The formation of the surface-attached layer is studied as a function of activation conditions, especially the temperature and the wavelength of the light used in the process.



INTRODUCTION

The structure and chemical composition of the surface of a given material frequently determines its performance when this material comes into contact with its surrounding environment.^{1–3} Accordingly, much effort has been made to generate surfaces with tailor-made properties. Pathways that have been elucidated in the past years are the attachment of self-assembled monolayers^{4–9} or the generation of chemically bound monomolecular layers. The latter processes range from the binding of polymers containing reactive sites^{10–15} to the generation of polymer brushes through surface-initiated polymerization.¹⁶

An interesting novel approach is based on the use of thermo or photoactive moieties for the chemical attachment of polymer layers onto a substrate. Here, the reactive groups are incorporated in the side-chains of the polymer or in a self-assembled monolayer. Upon thermal or photochemical activation of such groups, the polymer layer is attached to the surface or the polymer network is formed. A schematic representation of the process is depicted in Figure 1. For instance, sulfonyl azides decompose at appropriate temperatures into very reactive nitrenes that can establish covalent bonds with neighboring groups.^{17,18} In another case, benzophenone units are photochemically excited into a diradicaloid triplet state upon irradiation with ultraviolet light. Through radical abstraction and radical recombination, the benzophenone groups react with neighboring molecules.^{19,20}

For both systems, the process has proven to be quite universal and almost all polymers can be used.

In an effort to explore new methods for the surface immobilization of polymer layers, and to extend the scope of the cross-linkers, we here describe a new approach based on the insertion of reactive carbenes into C–H bonds. α -Diazoester groups are excellent carbene precursors²¹ and are readily available through a variety of synthetic routes.²²

For the immobilization of ultrathin layers, we describe the synthesis of a chlorosilane compound bearing such α -diazoester groups, the decoration of silicon substrate surfaces with these molecules, and the thermal attachment of polymer molecules coated onto the thus-obtained surfaces. For the preparation of polymer networks, we describe the synthesis of functionalized polymers containing pendant diazoester groups and their corresponding cross-linking and attachment process by activation with UV-light or heat.

EXPERIMENTAL SECTION

Materials. Allyl bromide, *N*-Boc-tyrosine methyl ester, chlorodimethylsilane, triethylamine, methanol, toluene, platinum activated on charcoal (10% Pt/C), isoamyl nitrite, trifluoroacetic acid (TFA), acetic acid (AcOH), methacryloyl chloride were obtained from commercial sources (Sigma-Aldrich). Triethylamine (NEt₃) was distilled (bp 90 °C) from CaH₂ prior to use and kept under inert atmosphere. Toluene

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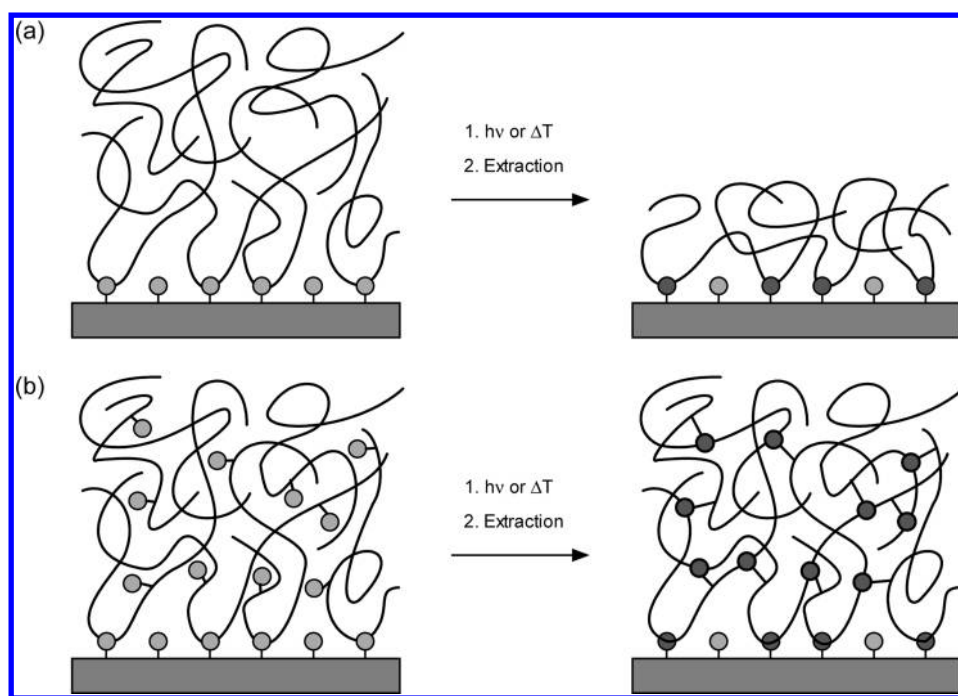


Figure 1. Schematic depiction of the strategy to obtain (a) polymer monolayers and (b) surface-attached polymer networks.

was dried over Na metal using benzophenone as indicator. All other chemicals and solvents (HPLC grade) were used as received. Polystyrenes (PS) of known molecular weight were purchased from Polymer Standard Service (Mainz, Germany), poly(sodium 4-sulfostyrene) (PS-SO₃Na) ($M_w = 2 \times 10^5$ and 1×10^6) and poly(2-ethyl oxazoline) (PEOX) ($M_w = 2 \times 10^5$ and 5×10^5) were purchased from Aldrich Chemical Co.

Methods. NMR spectra were recorded on a Bruker DPX 250 spectrometer using CDCl₃ as solvent, and TMS as internal reference. Transmission FTIR spectra of the attached polymer layers were recorded using a Biorad Excalibur Spectrometer. The dry thickness of coated polymer layers was measured by ellipsometry (Riss EL-X1). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Perkin-Elmer PHI 5600 spectrometer equipped with a concentric hemispherical analyzer and using an Al K_α X-ray source. The contact angle measurements were carried out on an OCA 20 system from Dataphysics GmbH, using Millipore-filtered water as a test liquid. The deposited volume of the drop was 3.0 μL with a dropping rate of 0.1 μL/s using a syringe pump.

Synthesis of *O*-Allyl *N*-Boc-tyrosine Methyl Ester (1). This compound was synthesized according to published procedures.²³ In a typical run, 5.0 g (16.9 mmol) *N*-Boc Tyrosine methyl ester and 3.2 mL (37.2 mmol) allyl bromide were dissolved in 5 mL of acetone and 2.8 g (4.0 mmol) of potassium carbonate was added. The mixture was heated to reflux for 16 h and then cooled to room temperature. Dichloromethane (100 mL) was added and the organic solution was hydrolyzed twice with 100 mL of water. The aqueous phase was washed twice with 75 mL of dichloromethane. The combined organic phases were washed twice with 100 mL of aqueous NaOH (10%) and dried over anhydrous Na₂SO₄, and the solvent was evaporated. The resulting product was purified by column chromatography using dichloromethane as eluent. Yield 5.4 g (95%).

¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.03 (d, $J = 8.7$ Hz, 2H, C_{ar}-H), 6.84 (d, $J = 8.7$ Hz, 2H, C_{ar}-H), 6.05 (ddt, $J = 17.2$, 10.5, and 5.3 Hz, 1H, O-CH₂-CH=CH₂), 5.40 (dq, $J = 17.2$ and 1.5 Hz, 1H), 5.28 (dq, $J = 10.5$ and 1.5 Hz, 1H), 4.95 (m, 1H, NH-Boc), 4.57–4.51 (m, 1H, CH-NH-Boc), 4.51 (dt, $J = 5.3$, 1.5 Hz, 2H, O-CH₂-CH=), 3.71 (s, 3H, O=C-O-CH₃), 3.11–2.92 (m, 2H, CH₂-CH-NH-Boc), 1.42 (s, 9H, (CH₃)₃C-O).

¹³C NMR (63 MHz, CDCl₃) δ (ppm): 172.5 (CH₃O-C=O), 157.7 (C_{ar}-O), 155.1 (NH-CO-O), 133.3 (-CH=CH₂), 130.3 (C_{ar}-

CH₂-CH-NH), 128.2 (CH-C_{ar}), 117.6 (CH₂=CH-CH₂), 114.8 (CH-C_{ar}-O), 79.9 (O-C-(CH₃)₃), 68.8 (CH₂-CH=CH₂), 54.6 (CH-NH), 52.2 (-O-CH₃), 37.5 (CH₂-CH-NH), 28.3 (C-(CH₃)₃).

Synthesis of *O*-(3'-(Chlorodimethylsilyl)propyl *N*-Boc-tyrosine Methyl Ester (2). Standard hydrosilylation procedures^{24,25} were employed for the synthesis of this compound. Typically, 5.1 g of 1 (16.1 mmol) were placed in a round flask and 50 mL of freshly distilled chlorodimethylsilane (bp 35 °C) were added along with a catalytic amount of 10% of Pt/C under a nitrogen atmosphere. This mixture was stirred at 40 °C overnight. After that, the catalyst was filtered off and the excess of chlorodimethylsilane was removed by vacuum distillation yielding the desired product 2 in quantitative yields.

¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.02 (d, $J = 8.6$ Hz, 2H, C_{ar}-H), 6.81 (d, $J = 8.6$ Hz, 2H, C_{ar}-H), 4.94 (m, 1H, NH-Boc), 4.59–4.46 (m, 1H, CH-NH-Boc), 3.92 (t, $J = 6.5$ Hz, 2H, O-CH₂-CH₂-CH₂), 3.71 (s, 3H, O=C-O-CH₃), 3.09–2.93 (m, 2H, CH₂-CH-NH-Boc), 1.97–1.82 (m, 2H, -O-CH₂-CH₂-CH₂-Si), 1.42 (s, 9H, (CH₃)₃C-O), 1.06–0.91 (m, 2H, CH₂-Si-Cl), 0.44 (s, 6H, -Si(CH₃)₂).

Immobilization of 2 on Silicon Wafers. The silicon substrates were cleaned in an ultrasonic bath in methanol for 5 min. The substrates were placed in a Schlenk tube and dried in vacuum. Then the flask was purged with nitrogen and the substrates were completely covered with dry toluene; 5.0 mL of a solution of 2 in toluene (0.1 mol/L) and a few drops of NEt₃ were added under inert atmosphere and the samples were left to stand overnight. After reaction, the samples were extensively cleaned by rinsing with toluene and ethanol and dried with dry nitrogen.

Deprotection: Removal of the Boc Groups from the Polymer Monolayers. The functionalized substrates were placed in a Schlenk tube and covered with 5.0 mL of a solution of CH₂Cl₂/CF₃CO₂H (ratio 2:1). After incubation at room temperature for 1 h, the substrates were extensively washed with CH₂Cl₂ and then ethanol and dried in a stream of dry nitrogen.

Diazotation of α -Aminoesters (3) Monolayers. The surfaces functionalized with polymer containing α -aminoester groups (3) were placed in a Schlenk tube and covered with a solution of 60 mL of CHCl₃, 1.4 mL of NEt₃, 0.2 mL of CH₃CO₂H and 1.8 mL of isoamyl nitrite. The reaction vessel was heated to 60 °C for 90 min. After

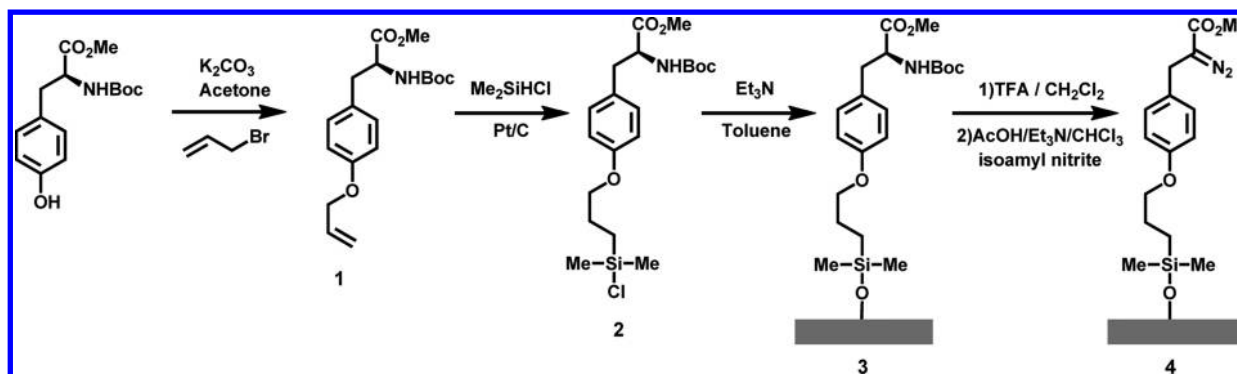


Figure 2. Synthesis of silicon surfaces decorated with a monolayer of the α -diazoester 4.

this period, the substrates were washed several times with chloroform and ethanol and finally dried in a stream of nitrogen.

Synthesis of *O*-Methacryloyl *N*-Boc-tyrosine Methyl Ester (5). In a typical run, 1.0 g of methyl ester of *N*-Boc-tyrosine and 0.56 mL of NEt_3 were dissolved in 40 mL of CHCl_3 . This solution was cooled in an ice-bath. Then a solution of 0.33 mL of methacryloyl chloride in 2 mL of CHCl_3 was added dropwise. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was followed by TLC. The reaction mixture was then hydrolyzed and washed several times with water (3×50 mL) in order to remove unreacted methacryloyl chloride. The organic phase was dried over anhydrous sodium sulfate. After that the drying agent was filtered off and the organic solvent was evaporated. The final product was purified by column chromatography using dichloromethane as eluent. (Yield 90%)

^1H NMR (250 MHz, CDCl_3) δ (ppm): 7.15 (d, $J = 8.6$ Hz, 2H, $\text{C}_{\text{ar}}\text{-H}$), 7.05 (d, $J = 8.6$ Hz, 2H, $\text{C}_{\text{ar}}\text{-H}$), 6.33 (p, $J = 1.0$ Hz, 1H, $(\text{CH}_3)\text{-CH=CHH}$), 5.75 (p, $J = 1.5$ Hz, 1H, $(\text{CH}_3)\text{-CH=CHH}$), 4.97 (br, 1H, NH-Boc), 4.66–4.51 (m, 1H, CH-NH-Boc), 3.71 (s, 3H, O=C-O-CH_3), 3.13–3.04 (m, 2H, $\text{CH}_2\text{-CH-NH-Boc}$), 2.05 (dd, $J = 1.5$ and 1.0 Hz, 3H, $(\text{CH}_3)\text{C=CH}_2$), 1.42 (s, 9H, $(\text{CH}_3)_3\text{C-O}$).

^{13}C NMR (63 MHz, CDCl_3) δ (ppm): 172.3 ($\text{CH}_3\text{O-C=O}$), 165.9 (O-CO-C=CH_2), 158.5 (NH-CO-O), 150.1 ($\text{C}_{\text{ar}}\text{-O}$), 136.1 ($\text{C}_{\text{ar}}\text{-CH}_2$), 133.7 ($\text{OC-C}(\text{CH}_3)=\text{CH}_2$), 130.4 ($\text{CH}_2=\text{C}(\text{CH}_3)$), 127.4 (CH-C_{ar}), 121.8 (CH-C_{ar}), 80.2 ($\text{O-C}(\text{CH}_3)_3$), 54.5 (CH-NH), 52.4 (O-CH_3), 37.9 ($\text{CH}_2\text{-CH-NH}$), 28.4 ($\text{C}(\text{CH}_3)_3$), 18.5 ($\text{CH}_3\text{-C=CH}_2$).

General Procedure for Polymerization Reactions. To carry out the polymerizations the monomers were dissolved in an appropriate solvent under inert atmosphere: styrene or methyl methacrylate in DMF, dimethyl acrylamide or acrylic acid in methanol. The final concentration was set to 1 mol/L and 0.1 mol % of AIBN was added as initiator. The solutions were placed in a Schlenk tube and were then degassed by five freeze–thaw cycles. Finally the mixture was heated to 60 °C for 16 h. The reactions were stopped by precipitating the mixture in a cold nonsolvent for the corresponding polymer, PS or PMMA in methanol and PDMAA, PAA in diethyl ether. The copolymers were purified by precipitation using an appropriate solvent/nonsolvent mixture. Copolymers with 1, 2 and 5% of the cross-linking group were prepared.

Deprotection of Boc Group on Polymers (6). The functionalized polymers (6) were placed in a round-flask and dissolved in 25 mL of a solution of $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{CO}_2\text{H}$ (ratio 2:1). After incubation at r.t. for 1 h, the deprotected polymers were purified by precipitating them in a large excess (125 mL) of nonsolvent. After that, the polymers were dried in vacuum.

General Procedure of Diazotation of α -Aminoester Copolymer (6). The copolymers with α -aminoesters (6) were dissolved in a solution of 60 mL of CHCl_3 , 1.4 mL of NEt_3 , 0.2 mL of $\text{CH}_3\text{CO}_2\text{H}$ and 1.8 mL of isoamyl nitrite and heated to 60 °C for 90 min. After this period, the polymers were precipitated in a large excess of

nonsolvent. The polymers were then further purified by precipitation and finally dried in vacuum.

Preparation of Polymer Layers. Thick overcoats (>100 nm) of polymer were deposited onto the silane modified substrates by spin-coating solutions of the copolymers at 3000 rpm for 60 s. The copolymers were dissolved in toluene (PS and PMMA), methanol (PAA) or isopropanol (PDMAA) at concentrations of 20 mg/mL. The samples were dried in air and used directly for the cross-linking experiments. These experiments were carried out at room temperature using two different wavelengths (250 and 365 nm) for selected periods of time. After illumination, the samples were extracted in a Soxhlet apparatus with a good solvent for the corresponding copolymers for 18 h to remove nonbonded polymer.

Determination of Gel Content. A Heraeus vacutherm oven preheated to the desired temperature was used for the experiments on thermal cross-linking. After heating for preselected periods of time, the samples were cooled back to room temperature and the thickness of the coated film was measured by ellipsometry. After that, the samples were extensively washed using a Soxhlet apparatus, with a good solvent for the coated polymer and the layer thickness again measured. The gel content is defined as the ratio of layer-thickness after extraction to the layer-thickness directly after heating.

RESULTS AND DISCUSSION

Silicon wafers decorated with the α -diazoester of tyrosine (4) can be prepared following the procedures schematically shown in Figure 2. The first step is the synthesis of a coupling agent precursor. This molecule can be obtained from the methyl ester *O*-allyl tyrosine through an ether coupling to 1 and hydrosilation. For the hydrosilation reaction platinum on charcoal (Pt/C, 10% Pt) was used as the catalyst. The use of the standard catalyst hexachloroplatinic acid (H_2PtCl_6) in this step should be avoided as it leads to a rapid reduction of the ester groups.²⁴

The chlorosilane 2 can be immobilized on SiO_2 surfaces by immersing an appropriate substrate into a dilute (typically 10^{-3} M) solution of 2 in toluene using few drops of dry NEt_3 as catalyst and acid scavenger. These surfaces decorated with α -aminoesters can then be turned into the desired α -diazoesters following standard deprotection and diazotation protocols. These procedures yield monolayers of the α -diazoester silane 4 having a typical thickness of ca. 1 nm.

Subsequently, thin polymer layers were then deposited on the α -diazoester decorated surfaces by spin-coating. To avoid artifacts caused by a inhomogeneous polymer coverage we typically deposited rather thick films with thicknesses of $d > 100$ nm. To induce the attachment reaction the samples were thermally annealed at a given temperature for the desired period of time.

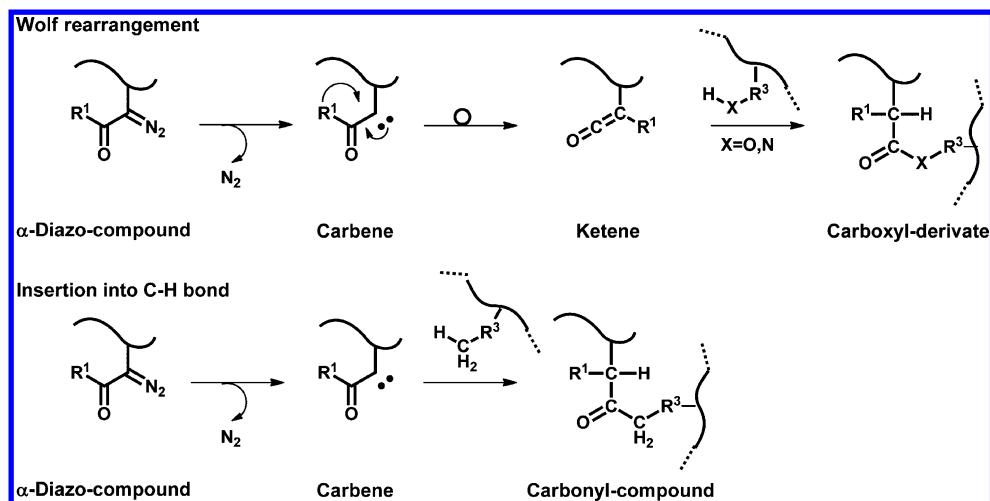


Figure 3. Carbene insertion into an O–H or N–H bond through Wolff rearrangement and insertion into a neighboring C–H bond.²²

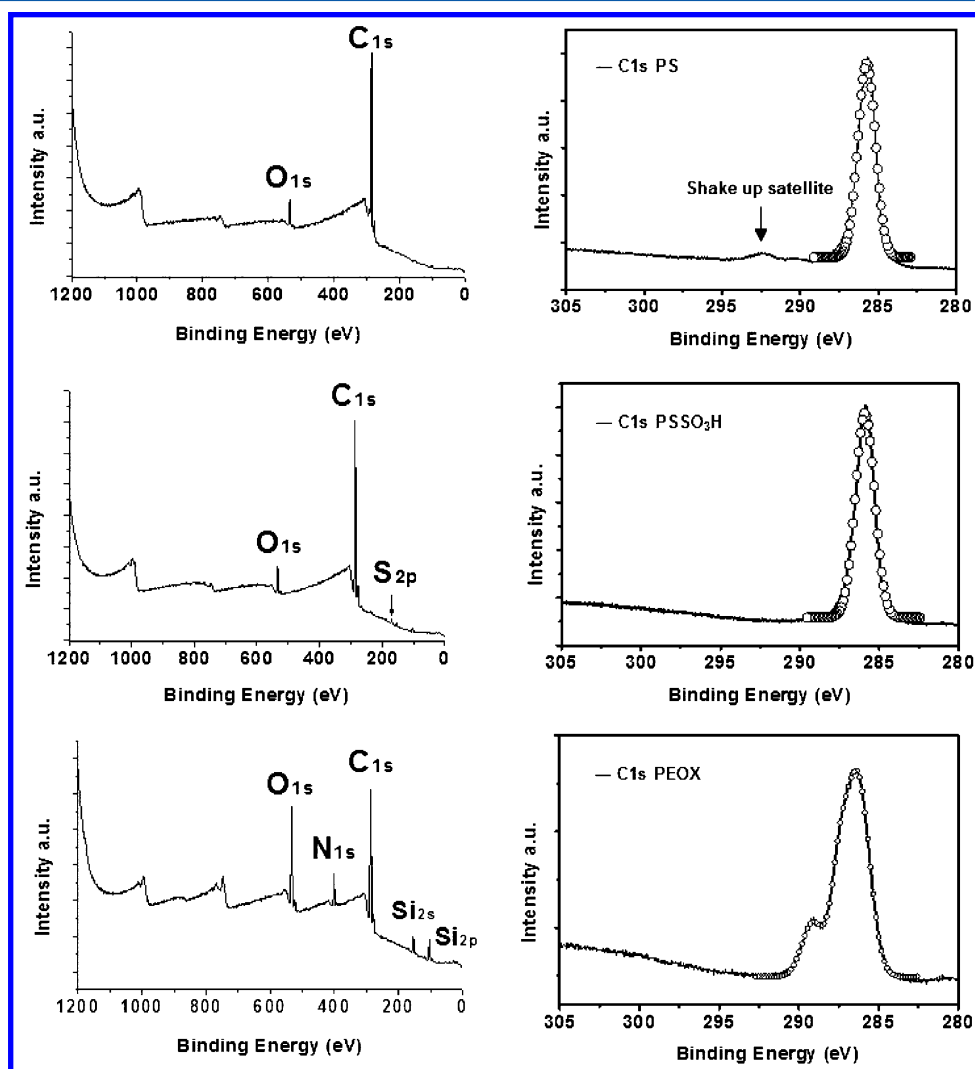


Figure 4. Survey XPS-spectra and C1s detail spectra from surfaces coated with polymer monolayer of (a) polystyrene, (b) poly(styrene sulfonate) PS-SO₃Na, and (c) poly(ethylenoxazoline) (PEOX).

The thermal decomposition of α -diazoesters and subsequent reactions of the obtained reactive intermediates are well described in the literature.²⁶ Briefly, upon heating the α -diazoester groups lose nitrogen and form an alkylcarbene.

This reactive carbene can insert into an X–H bond of an adjacent organic molecule, such as alkyl (C–H), alcohol or acid (O–H), amines or amides (N–H). In the literature, two different reaction mechanisms have been discussed, one

through Wolff rearrangement to a ketene, which can then insert, or a direct insertion.²² Both options are schematically shown in Figure 3.

We have performed various sets of experiments using three model polymers for surface-attachment through diazo chemistry. Aside from the investigation of suitable reaction parameters we aimed at demonstrating the versatility of this novel family of thermal cross-linkers. As examples we chose: hydrophobic polystyrene, hydrophilic poly(ethylenoxazoline) (PEOX) and as an example for a charged polymer poly(styrenesulfonate) PS-SO₃Na.

The attached monolayers were characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. As depicted in Figure 4, the spectra present the expected chemical composition for every deposited polymer. The XPS spectrum of PS shows a strong C1s signal at (285.5 eV) and a typical shakeup shoulder at 292.5 eV, for the PS-SO₃H monolayer signals corresponding to oxygen (532.7 eV, O1s), carbon (286.4 eV, C1s) and sulfur (169.3 eV, S2p) can be identified and finally the PEOX monolayer shows the expected signals from oxygen (532.8 eV, O1s), nitrogen (401.6 eV, N1s) and carbon (286.4 eV, C1s).

For the particular case of PEOX, the relative intensities of the signals ascribed to carbonyl (C=O) and C-C + C-N to total C1s were as follows: 15.8% at 289 eV and 84.2% at 285 eV. C=O/C-C + C-N peak area ratios were close to the theoretical values proving that indeed the PEOX was thermally attached onto the silane-modified surface.

After the chemical characterization of these surface-attached monolayers, in the first set of experiments we have varied the annealing time of the thermochemical process while keeping the temperature constant at 120 °C. The heating time varied between 1 and 20 min. After heating, all the samples were rigorously extracted with toluene or methanol in a Soxhlet apparatus (18 h) to remove nonbonded chains. The variation of the polymer thickness with heating time is depicted in Figure 5.

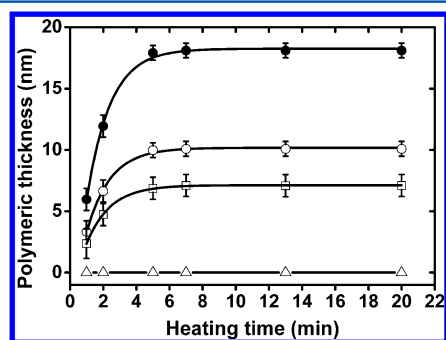


Figure 5. Influence of heating time on the thickness of surface-attached monolayers of PS (●), PS-SO₃Na (○), and PEOX (□) using SiO₂ surfaces carrying a self-assembled monolayer of the α -diazo coupling agent and uncoated SiO₂ surfaces (Δ) as a reference system.

The thickness of the surface-attached monolayer increases with heating time reaching a constant value of 7 nm, 10 and 18 nm for PEOX, PS-SO₃Na and PS, respectively. These saturation values are reached after 5 min under the described conditions.

To prove that the formation of these ultrathin attached polymer films is indeed due to the thermal activation of the α -diazoester units of the decorated surfaces we have deposited polymer layers on nonfunctionalized silicon wafers as a reference system and followed the same protocol for the

attachment reaction. However, in this case the layers were completely washed off during extraction.

In the next set of experiments, we have investigated the influence of the molecular weight of the deposited polymer on the thickness of the chemically attached monolayers. Here we used polystyrenes with narrow polydispersities ($PDI \leq 1.11$) and different molecular weights, which varied from 3×10^4 to 3×10^6 g mol⁻¹. A thick polymer layer was deposited on functionalized substrates and heated up to 120 °C for 20 min. After exhaustive washing with toluene, the monolayer thickness (d_{max}) was measured by ellipsometry. As shown in Figure 6a, the thickness d_{max} of the attached layers increases with increasing molecular weight of the deposited polymer. As it has been already discussed for the from a conceptual point of view rather similar benzophenone,¹⁹ and sulfonyl azide¹⁸ chemistries the thickness of the chemisorbed polymer layer depends on the radius of gyration of the deposited polymer, which scales^{27,28} with $R_g \approx (M_w)^{1/2}$. The reason for this behavior is that all molecules, which are bound in the monolayer formation process, have to be in contact with the surface groups.

The same tendency has been observed for PEOX and PS-SO₃H: increasing the molecular weight of the polymer implies thicker monolayers. In Table 1, the thicknesses of monolayers are shown for those polymers.

Preparation of Surface-Attached Polymer Networks Bearing α -Diazoester Groups. A strategy, which allows for the generation of thicker surface-attached layers is the generation of surface-bound polymer networks. To this polymers were generated, which carried the appropriate groups as side chains. Such polymers 7 can be synthesized by copolymerization of a precursor monomer 5 with an appropriate comonomer (Figure 7).

The first step is the preparation of a protected tyrosine with a polymerizable moiety 5. This compound can easily be copolymerized with other comonomers using AIBN as initiator. The α -aminoester copolymer 6 can be converted into α -diazoester copolymer 7 via standard deprotection and diazotation protocols. Following this route, diazoester groups were incorporated into a variety of polymers such as PMMA or PS, poly(dimethyl acrylamide) (PDMAA) or poly(*N*-isopropyl acrylamide) (PNIPAM) or polymers with charged groups like PSSNa. The cross-linker content could be varied by adjusting the comonomer ratio. Typical contents of the polymer used in this study ranged from 1 to 5%. The average molecular weight (M_n) of the synthesized copolymers varied from 1×10^5 to 3×10^5 g/mol, which means that between 10 and 50 α -diazo groups are incorporated into each polymer chain. This is more than sufficient to allow for an efficient cross-linking.

After the preparation of the copolymers carrying the diazo groups, the influence of the *cross-linking temperature* on the thickness of the attached-polymer layer has been studied. To this the polymer layers were first coated onto silicon surfaces decorated with diazo anchors and then heated to different temperatures between 80 and 180 °C for 10 min. During this thermal activation the diazo groups from the surface and from polymer chains in the coated layers are decomposed and a simultaneous cross-linking process and covalent attachment to the surface takes place. To guarantee complete removal of all polymer chains not covalently bound to the polymer network, after thermal activation all samples were rigorously extracted for 16 h with a good solvent for the respective polymer using a Soxhlet apparatus.

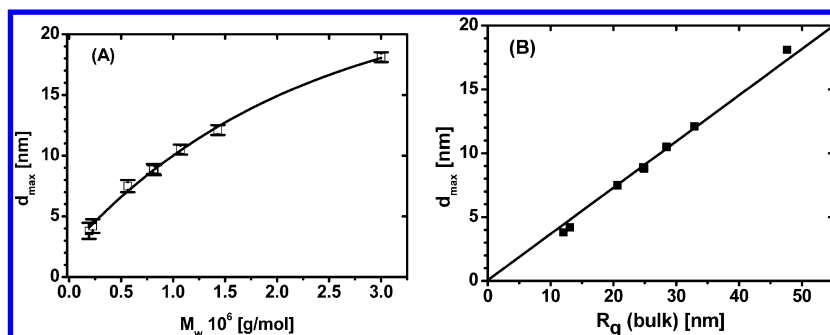


Figure 6. Influence of the molecular weight of the deposited polymer on the thickness of the surface-attached polystyrene monolayer. (A) Influence of the molecular weight of the attached polymer on the saturation thickness. (B) Relation between the thickness of the surface-attached monolayers and the radius of gyration of the deposited polymers.

Table 1. Variation of d_{\max} with the Molecular Weight for PEOX and PS-SO₃Na

polymer	M_w [g/mol]	d_{\max} [nm]
PEOX	2×10^5	3.2 ± 0.8
PEOX	5×10^5	7.1 ± 0.6
PS-SO ₃ Na	2×10^5	4.0 ± 0.6
PS-SO ₃ Na	1×10^6	10.1 ± 0.4

Figure 8 compares the cross-linking behavior of PNIPAM with α -diazoester moieties and the corresponding nonfunctionalized PNIPAM as a control; the heating time was set to 10 min. In the case of the α -diazoester containing polymers complete cross-linking (i.e. gel content of 100%) was reached within the given time frame when the temperature was higher than 120 °C, while unmodified PNIPAM created only a chemically attached monolayer. The thickness of this monomolecular layer was 5 nm and remained constant regardless of the annealing temperature. This is direct evidence that the formation of the polymer network takes place due to the incorporation of these reactive groups into the polymer chain and is not caused by heat induced side reactions.

In order to elucidate the kinetics of the cross-linking process, in the following set of experiments we chose PMMA with 5% of 7 as the standard polymer. Heating the polymer layers to a given temperature, the variation of the gel content with respect to the heating time has been determined. Figure 9 shows the gel content for three different temperatures. At temperatures of 120 °C or higher, a complete cross-linking of the polymer is achieved within a few minutes, whereas a very slow cross-linking process takes place at 100 °C. However, complete cross-linking is still reached after 2 h at this temperature.

Cross-linking by Photoactivation of Polymers with Diazoester Moieties. Aside from thermal activation, α -

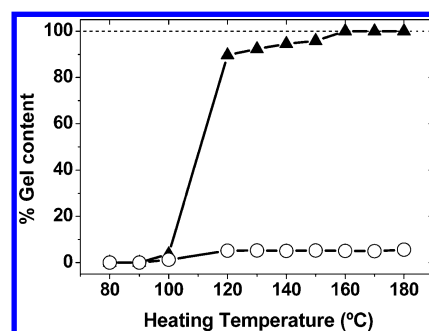


Figure 8. Variation of gel-content of PNIPAM based polymer layers of 7 on silicon substrates covered with 4 as a function of the annealing temperature; annealing time was 10 min; polymer with (\blacktriangle) and without (\circ) diazoester moieties.

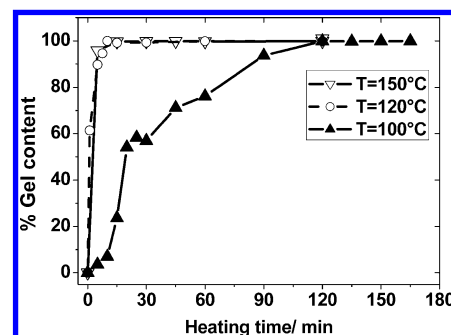


Figure 9. Variation of the gel content with the heating time of PMMA layers (thickness 100 nm) containing 5% of 7.

diazoesters can also be photochemically triggered. This property is of special interest if good spatial control of the surface chemistry is required.

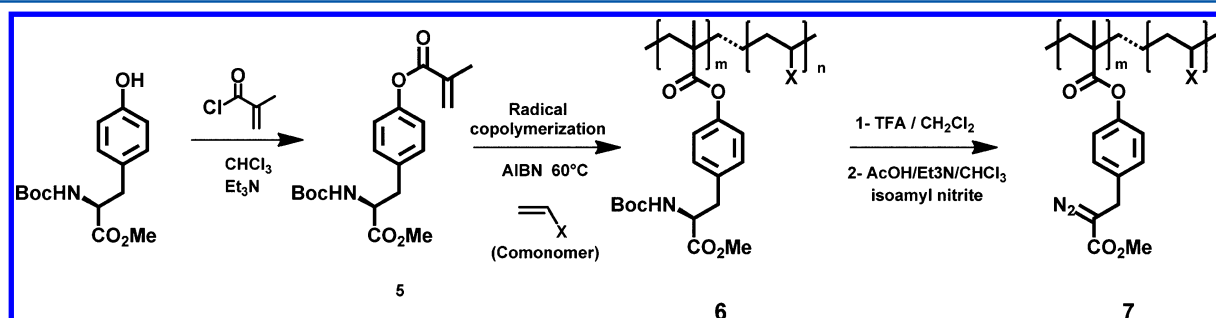


Figure 7. Synthetic route toward α -diazoester group containing copolymers 7.

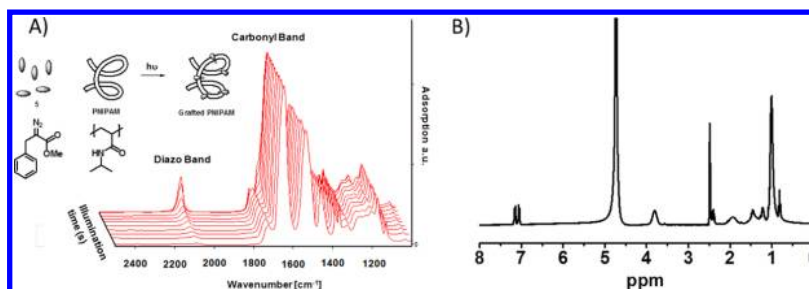


Figure 10. (A) Variation of the FTIR-spectra with reaction time of the model molecule (8) mixed with PNIPAM. Each spectrum was acquired after 15 s of irradiation with UV-light at 250 nm. (B) NMR-spectrum of PNIPAM grafted with a diazoester derivate of phenylalanine (8).

In order to study the suitability of the diazoester moieties as photo-cross-linkers, we have, in a first step, prepared a model system where a small molecule bearing a diazoester group was mixed with a polymeric matrix and illuminated with UV-light. This induces the decomposition of the diazo group and a corresponding binding of the molecule to the polymeric chain. The selected model molecule is the diazoester derivate of phenylalanine (8), as the polymeric matrix we have selected PNIPAM. The grafting reaction was followed by FTIR spectroscopy. The variation of the intensities of the FTIR-bands with respect to the illumination time is depicted in Figure 10a. All spectra were normalized with respect to the carbonyl band at 1650 cm^{-1} , because this signal remains constant during the grafting reaction. As shown in Figure 10a, the band at 2090 cm^{-1} , which can be attributed to the diazo bonds, decreases during illumination ($\lambda = 250\text{ nm}$). The NMR-data obtained from the grafted PNIPAM shows signals around 7 ppm, which belong to the aromatic units of the attached α -diazoester moieties (Figure 10b). For longer wavelengths (365 nm), no significant reaction between the photophore group and the polymer was observed, and the ratio between the carbonyl and diazo band remains almost constant. According to these results, the photoactivation of the label molecule and its subsequent grafting to the polymer chain takes place in short periods of time using short wavelengths for UV illumination. The model study also indicates that the photochemical reaction is a rather clean process and no larger number of byproducts is formed.

After this preliminary study, copolymers functionalized with diazo moieties were photochemically cross-linked. The content of the diazo units in the PMMA copolymer was determined by FTIR spectroscopy using the diazo stretching vibration.

These functionalized copolymers were coated onto modified silicon surfaces (decorated with the same photophore) and the network formation and surface attachment was studied. The dried thickness of the coated polymer films was around 100 nm in all cases. The deposited polymer layers were cross-linked and simultaneously covalently attached to the functionalized surface by UV-illumination at 250 nm for 4 min. It has been reported that the reaction between a carbene and molecular oxygen may produce the corresponding carbonyl oxide, which is in equilibrium with dioxiranes and can also undergo further transformations upon irradiation with UV-light.^{29,30} To look into this issue, we have carried out the experiment, both under ambient conditions and under nitrogen atmosphere and no differences with respect to the degree of cross-linking (gel content), the behavior of the α -diazoesters decomposition and the finally obtained polymer network could be found. The activation process can be easily carried out in air and in a very simple way surface-attached polymer networks are obtained.

CONCLUSIONS

We have presented a new strategy for the generation of surface-attached polymer monolayers and networks based on a thermally or photochemically induced carbene intermediates followed by insertion reactions. For the generation of surface-attached polymer monolayers, first self-assembled silane monolayers carrying α -diazoester groups are prepared. When this layer is coated with a thin polymer film and either thermally or photochemically activated, surface-attached monolayers of these polymers are obtained. When the diazoester groups are placed as side groups of polymer chains, surface-attached polymer networks are formed. In both cases, nitrogen is cleaved off and the formed carbene intermediates can insert into any neighboring chain so that the layers are formed more or less independent from the chemical composition of the polymer. While the compounds can be easily handled at room temperature, already temperatures of $120\text{ }^{\circ}\text{C}$ are sufficient to induce film formation. Our data suggest a linear relationship between the dry thickness of attached polymer monolayer (d_{max}) and the polymer radius of gyration. This behavior is very similar to that of the conceptually similar formation of such polymer layers through benzophenone or sulfonyl azide chemistries. The incorporation of α -diazoesters into the polymeric chains can be easily achieved through copolymerization of an aminoester derivate monomer with a base comonomer, followed by a diazotation reaction of aminoester moieties. The cross-linking density can be controlled according to the comonomer feed ratio. Due to the covalent bonds between surface and polymer layer, the polymer network presents a high resistance against solvent exposure. The immobilization of this kind of scaffolds allows tailoring the chemical and physical properties of surfaces of many different types of materials, following a very simple way. The photochemistry of this group opens new avenues as the photoactivation process is very efficient at 250 nm and has good stability at 365 nm.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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