# Surface Attached Polymer Networks through Thermally Induced Cross-Linking of Sulfonyl Azide Group Containing Polymers

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ABSTRACT: We report on a simple and versatile way for the modification of surfaces with thin polymer films through the thermally induced generation of surface-attached polymer networks. The system is based on copolymers, which contain a thermally reactive sulfonyl azide derivative that has been incorporated into the polymer chain during a radical copolymerization reaction. The copolymers are spin-coated from solution onto a silicon-wafer, which had been previously modified with an organosilane. Upon heating the sulfonyl azide decomposes, leading to a C−H insertion reaction and, at sufficiently high conversion, network formation. As groups in the forming network also attack the molecules of the surface-attached monolayer, the forming network becomes directly attached to the substrate surface. Following this method thin layers of polymer networks from a variety of polymers with different properties can be attached to the substrate. Furthermore, the process can be used for the generation of microstructures of polymers in hot-embossing processes. Here, cross-linking occurs during the embossing process and dimensionally stable microstructures are formed.

## Introduction

The attachment of polymer networks to the surface of a material is a powerful means to control the interactions of a material with its environment. Layers from cross-linked polymer systems which are chemically bound to the surface of a material allow for tunable film thickness of the coating over a wide range, combined with mechanical and chemical stability. In addition networks have the ability of hosting functional groups with a variety of functionalities. Due to the variability of such systems it can be envisioned that they become used in a broad spectrum of applications ranging from biotechnology to microsystem engineering.[1−6]

Cross-linking of bulk polymers is one of the most common techniques in polymer science to stabilize shape and internal structure of objects and accordingly many methods have been reported on how to achieve well defined cross-linking processes.[7−13] To this two basic strategies are available: Network formation can be achieved through a cross-linking polymerization or cross-linking of preformed polymers. However, techniques for the generation of bulk polymer networks cannot be easily transferred to the preparation of networks in very thin films. For example, if surface initiated polymerization reactions are carried out with difunctional monomers or prepolymers, high monomer conversion within the thin layer is required to reach the gel point, which in turn requires significant experimental effort.[3,14] On the other side cross-linking of thin polymer films with low-molecular weight bifunctional agents simply mixed into the polymer to be cross-linked might lead to phase separation of the high and low molecular weight compounds and therefore inhomogeneous layers.[15,16]

Phase separation can be avoided if the groups (frequently referred to as ‘curing agents’) involved in the cross-linking are covalently attached to the polymer chains. As schematically shown in Figure 1a, linking to a neighboring polymer chains can occur as the result of the chemical reaction of two different functional groups on different polymer chains, e.g. through a condensation reaction, a photo dimerization, a thermal [4 + 4]-cycloaddition or other addition-reactions such as “click-chemistry”.[2,5,17−24] However, to reach a sufficient cross-link density, this curing-method requires a significant density of the functional groups in the polymer, which leads to changes in the physical properties of the material. At low density, especially if the polymer contains less than 1% of such functional groups, however, the probability that they ”find” each other will be very low, leading to low cross-linking densities while a significant number of unreacted groups pertain in the film.

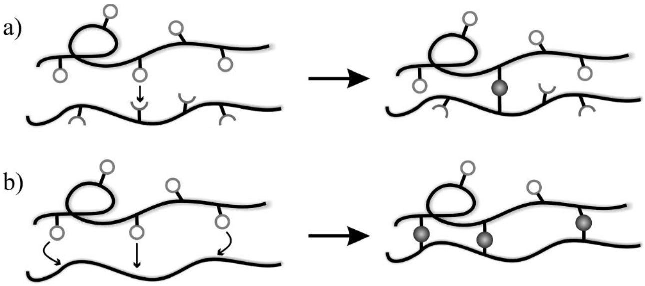

**Figure 1.** Illustration of different approaches to cross-link polymer chains: (a) Reaction between two functional groups of different polymer chains. (b) Cross-link formation due to the reaction between one functional group and the C−H bonds in the neighboring polymer chain.

An alternative strategy, followed in this publication, is schematically depicted in Figure 1b. Here, the cross-linker groups are incorporated as side-chain of the polymer and react with the backbone of the neighboring chains through insertion into C−H-bonds contained in those chains. For clarity reasons the attack of photoactive groups onto segments of the own chain, which would lead to loop formation, is omitted in the figure. The insertion process does not require the presence of any functional groups in close proximity of the activated site and is accordingly rather independent from the peculiarities of the polymer structure. For photochemical curing this method has been realized using benzophenone or arylazide groups, as well as acyl ketones.[1,4,25−29]

Although photo-cross-linking is a convenient reaction, for systems in which the layer has no access to light, a thermal process would be desirable which follows a C−H insertion mechanism. In this respect Hawker and co-workers describe a first experiment using a polystyrene polymethylmethacrylate

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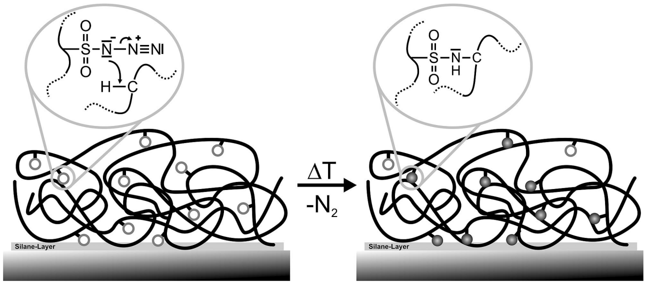


**Figure 2.** General scheme of the preparation of surface-attached polymer networks with sulfonyl-azide containing polymers via heat treatment. Covalent binding between the polymer chains and to the surface occurs in one step.

copolymer carrying benzylazide groups at a cross-linking temperature of 250 °C.[30]

In this paper we describe the thermal generation of surface-attached polymer networks based on the curing mechanism shown in Figure 1b.

Since the seminal work of Breslow et al. in the 1960s it is well-known that sulfonyl azide groups cleave off nitrogen and form a nitrene when raised to sufficiently high temperature. The nitrene has a high tendency to insert into almost any C−H bonds and in some cases even O−H-bonds.[31−34] Besides this, sulfonyl azides are rather robust compounds so that monomers carrying such moieties can be used in a standard free radical (co)polymerization procedure. This in turn allows to synthesize azide group containing polymers in a straightforward manner. After spin-casting of the obtained polymers from solution onto an organic surface, such as an octadecyltrichlorosilane- (OTS-) modified silica-surface, network-generation and surface attachment occurs upon heating of the sample as shown in Figure 2. We describe the synthesis of such polymers and networks and how such materials can be used to obtain dimensionally stable polymeric microstructures (thermosets).

## Experimental Section

**Materials.** All monomers were dried with $CaH_2$ and distilled under nitrogen with reduced pressure. AIBN was recrystallized from ethanol. Toluene was distilled from molten sodium using benzophenone as indicator. Triethylamine was distilled from calcium hydride. All other chemicals and solvents (HPLC grade) were used as received. Silicon substrates were cleaned in an ultrasonic bath in methanol and toluene (5 min each).

**Synthesis of 4-Styrenesulfonyl Chloride (1).** Na-4-styrenesulfonate (14.7 g; 72.6 mmol, 1.00 equiv) was suspended under nitrogen in DMF (75 mL) and cooled to 0 °C. Afterward thionyl chloride (32 mL, 441 mmol, 6.08 equiv) was added dropwise within 10 min. The reaction mixture was stirred at 0 °C for 30 min and subsequently at room temperature for 1 h, during which a homogeneous solution was obtained. The solution was poured onto ice (380 g), and the resulting aqueous layer was extracted with diethyl ether (3 × 80 mL). The combined organic layers were dried with $Na_2SO_4$ and the solvent was evaporated. After drying in vacuum, the resulting pale yellow oil (10.7 g, 52.8 mmol, 73%) was used in the next step without further purification. $R_f = 0.49$ (hexane/ethyl acetate = 10:1). $^1$H NMR (250 MHz, $CDCl_3$), $\delta$ (ppm): 7.99 (d, $J = 8.8$ Hz, 2H, C−$H_{ar}$), 7.61 (d, $J = 8.5$ Hz, 2H, C−$H_{ar}$), 6.78 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, −C*H*=$CH_2$), 5.96 (d, $J$= 17.5 Hz, 1H, −CH=CH$H_{cis}$), 5.54 (d, $J = 11.0$ Hz, 1H, −CH=CH$H_{trans}$). $^{13}$C NMR (63 MHz, $CDCl_3$), $\delta$ (ppm): 144.4 ($C_{ar}$−$SO_2N_3$), 142.9 ($C_{q,ar}$), 134.7 (−*C*H=$CH_2$), 127.4 (2 × $C_{ar}$), 127.1 (2 × $C_{ar}$), 119.3 (−CH−$CH_2$).

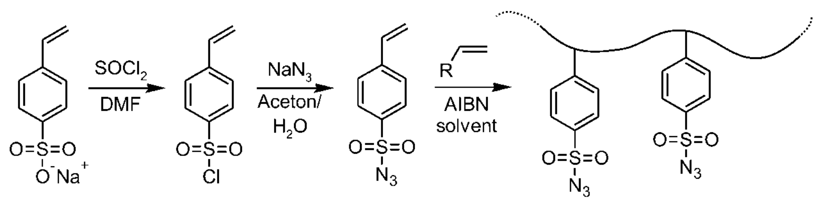
**Synthesis of 4-Styrenesulfonyl Azide (SSAz) (2).** Styrene sulfonyl chloride (**1**) (2.27 g, 11.2 mmol, 1.00 equiv) was dissolved in acetone (35 mL), and an aliquot volume of water (35 mL) was added. The turbid reaction mixture was cooled to 0 °C and $NaN_3$ (802 mg, 12.33 mmol, 1.10 equiv) was added in small portions. After the reaction mixture was stirred for 1.5 h at 0 °C, the acetone was removed in vacuum (30 °C, 150 mbar) and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over $Na_2SO_4$ and the solvent was evaporated at 30 °C. The resulting oil (2.19 g, 10.5 mmol, 94%) was dried in vacuum and used in the polymerization reactions without further purification. $R_f = 0.27$ (hexane/ethyl acetate = 15:1). $^1$H NMR (250 MHz, $CDCl_3$), $\delta$ (ppm): 7.91 (d, $J = 8.5$ Hz, 2H, C−*H*ar), 7.61 (d, $J$= 8.5 Hz, 2H, C−*H*ar), 6.78 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, −C*H*=$CH_2$), 5.95 (d, $J = 17.8$ Hz, 1H, −CH=CH$H_{cis}$), 5.52 (d, $J$= 10.8 Hz, 1H, −CH=CH$H_{trans}$). $^{13}$C NMR (63 MHz, $CDCl_3$), $\delta$ (ppm): 143.7 ($C_{ar}$−$SO_2N_3$), 136.7 ($C_{q,ar}$), 134.6 (−*C*H=$CH_2$), 127.6 (2 × $C_{ar}$), 126.9 (2 × $C_{ar}$), 118.6 (−CH−$CH_2$). FTIR (neat): 3092, 3069, 2348, 2129, 1593, 1491, 1398, 1372, 1167, 1089, 990, 928, 846, 748, 657, 591, 555 cm$^{-1}$. HRMS (EI): calcd for $C_8H_7SO_2N_3$, 209.2; found, 209.0. Anal. Calcd for $C_8H_7SO_2N_3$: C, 45.92; H, 3.37; N, 20.08; S, 15.29. Found: C, 45.25; H, 3.31; N, 19.53; S, 15.29.

**Polymerization.** In a typical run of the polymerization process, monomers were dissolved under nitrogen in an appropriate solvent (styrene, methyl methacrylate, 4-bromostyrene in toluene; *N*,*N*-dimethyl acrylamide, methacrylic acid, acrylic acid in methanol; styrenesulfonate in water/ethanol 3:1): The concentration was chosen to be 2 mol/L and 0.1 mol % AIBN was added. After five freeze−thaw-cycles, the solution was placed into a preheated water-bath (60 °C) for 20 h. The polymer was precipitated by dropwise adding a solution into a large excess of nonsolvent (PS, PMMA, PSBr in methanol; PDMAA, PMAA, PAA, PSSNa in diethyl ether) and filtered off. After drying it was taken up again in chloroform (PS, PMMA, PDMAA) or methanol (PMAA, PAA) and the precipitation procedure was repeated two more times. After that the polymers were dried in vacuum, water-soluble polymers were freeze-dried. The polymers were obtained as white powders with 30−60% yield with an $M_w$ of around 100 000−300 000 g/mol measured with GPC (PS and PMMA standards) and 300 000−500 000 (PMAA-standards). For PSBr, PDMAA, PAA, and PSSNa no appropriate standards were available, so that the given values should be taken only as a rough orientation. Details are given in the Supporting Information. DSC measurements (heating rate 10 K/min) showed a broad exothermic signal at 190 °C due to the azide decomposition. TGA experiments (heating rate 10 K/min) show a related mass loss in the same temperature region. As the molar concentration of the azide moieties is in most cases rather small, the $T_g$ of the copolymers have roughly the same values as the corresponding homopolymers. The copolymerization of MMA and styrenesulfonyl azide **2** was examined in further detail regarding the copolymerization parameters. It turns out, that the incorporation of the sulfonyl azide monomer is preferred (copolymerization parameters $r_{SSAz} = 5.81$, $r_{MMA} = 0.27$). The accordant copolymerization diagram is displayed in the Supporting Information.

**Immobilization of OTS on $SiO_2$ Surfaces.** Cleaned silicon wafers were placed into a Schlenk tube under nitrogen and covered with dry toluene. After adding a catalytic amount of $NEt_3$, a solution (50 mmol/L) of OTS in toluene was added (2.5 mL/wafer). This solution with the substrates was left at room temperature overnight and the samples were cleaned by rinsing extensively with dichloromethane, methanol and toluene.

**Preparation of the Polymer Layers.** Thin films of around 100 nm thickness were prepared by spin-casting solutions of the copolymers at 2500 rpm for 40 s. The copolymers were dissolved in toluene (PS, and PMMA), toluene/dioxane 8:2 (PSBr), methanol (PMAA, PAA), isopropanol (PDMAA) and water (PSSNa) at concentrations of 20 mg/mL. After spincoating, the samples were dried in air and directly used for the cross-linking experiments.

**Determination of Gel Content.** A Heraeus vacutherm oven was used for the cross-linking experiments, which was preheated to the desired temperature before the start of the reaction. After the sample was heated with the polymer layer for the desired time, it was cooled back to room temperature and the film thickness was measured with ellipsometry. For the calculation of the film thicknesses the



**1** **2**

**Figure 3.** Synthesis and copolymerization of 4-styrenesulfonyl azide.

bulk refractive indices of the respective polymers were taken (PMMA, $n = 1.49$, PDMAA, $n = 1.51$, PS, $n = 1.59$, and PSBr, $n = 1.61$; PMAA, PAA, $n = 1.51$, and PSSNa, $n = 1.55$).[35] Extraction of the samples in a good solvent (PS, PMMA in toluene; PMAA, PDMAA in methanol; PSSNa in water) for 16 h led to removal of any nonbonded polymer. After drying for at least 1 h at 60 °C the thickness of the resulting polymer layer was again determined with ellipsometry. The gel content is defined as the ratio of layer-thickness after extraction to the layer-thickness directly after heating.

**Hot Embossing.** Hot embossing was performed with a hot embossing machine from Schmidt. The polymer was ground into a fine powder with a mortar before putting it into the desired mold. A conventional 1 Euro Cent (feature size: 75 $\mu$m) was placed into the mold and the process was carried out under vacuum (1 mbar) as followed: The system was heated to 170 °C with a temperature rate of 10 K/min and kept at this temperature for 10 min. A pressure of 3 kN was then applied for 10 min. At this pressure, the system was cooled down with a temperature rate of 10 K/min and the sample was released.

## Results and Discussion

Sulfonyl azide monomer **2** can be obtained in high yields following two simple reaction steps as shown in Figure 3. First, styrenesulfonic acid sodium salt is transformed into the corresponding acid chloride with thionyl chloride, followed by chlorine-azide exchange with sodium azide. Due to great changes in the solubility of educts and products the resulting product is pure enough so it can be used in the polymerization step without additional purification. The following radical copolymerization at 60 °C with AIBN as an initiator poses no problems, because decomposition of the azide group only takes place at much higher temperatures (difference in the peak temperature in DSC experiments $\Delta T = 70$ °C at a heating rate of 10 K/min).[36]

Upon copolymerization, azide groups can be incorporated into a variety of polymers which were hydrophobic (PMMA, PS) or hydrophilic (PDMAA, PMAA, PAA, PSSNa) in nature or contained charged groups (PMAA, PAA, PSSNa). The azide contents could be varied from very low (1%) up to rather high functional group densities (20%). The molecular weight average ($M_w$) of the polymers ranged from 100 000 to 300 000 g/mol (300 000 to 500 000 g/mol for polyelectrolytes), which yields from 10 to 300 (30–500) azide groups per polymer chain, which is more than sufficient to cross-link the polymers. A determination of copolymerization parameters of P[MMA-*co*-SSAz] following the Finemann–Ross method for low conversion polymerization reactions showed, that the sulfonyl azide monomer is built into the polymer chain slightly preferentially compared to methyl methacrylate (MMA) ($r_{SSAz} = 5.81$, $r_{MMA} = 0.27$). Preferential incorporation was also observed with the other monomers, but not studied in detail.

The azide group contents of the PMMA-, PS- and PMAA-SSAz copolymers was determined by FT-IR-spectroscopy using the azide N–N=N stretching vibration to calculate the composition. The absorption coefficients were obtained in a separation calibration process. Elemental analysis confirmed the values of azide content from FT-IR-measurements and was the method of choice to determine the azide contents in PDMAA, PAA, and PSSNa copolymers.

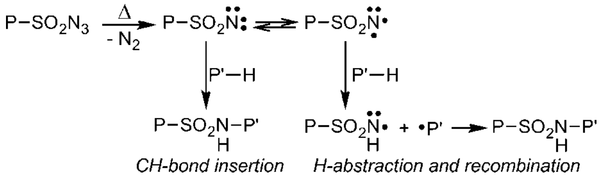


**Figure 4.** Reactions of singlet and triplet nitrenes obtained by the decomposition of polymeric sulfonyl azides. P = polymer chain.

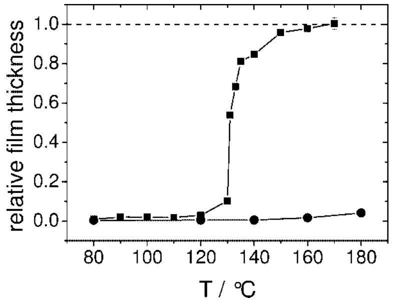


**Figure 5.** Cross-linking behavior of PMMA-layers with (■) and without (●) sulfonyl azide groups. The gelfraction was determined from the ratio of the film thickness of the samples after heating for 1 h at the given temperature to that after extraction in toluene for 16 h.

The obtained sulfonyl azide-containing polymers were deposited onto OTS-modified silicon wafers through spin-coating. The thickness of films used in this study was mostly around 100 nm. In the case of PAA and PSSNa polymers problems with dewetting occurred due to the strongly hydrophobic nature of the surface. Here either a different silane (methylacrylic benzophenone) was employed or a thin PMAA-network was first deposited and then used as a substrate for the following polymer deposition and cross-linking, i.e. used as an adhesion promoter.[37] In contrast to the work of Russell et al.,[24] the technique described here, provides covalent bonding to the surface and therefore has the potential of an increased stability of the surface-attached network layer, even when the network is strongly swollen. However, we did not compare the adhesion behavior of networks with and without the silane anchors in more detail.

Layers were cross-linked and covalently attached simultaneously by heating the samples in a conventional oven. It is known that aryl and sulfonyl azides can also be photochemically activated, but we focused our investigations here exclusively on the thermal process.[26,38–40]

The decomposition and binding mechanism of sulfonyl azides is well described.[31,33,41] Briefly, upon heating the sulfonyl azide groups loose nitrogen and form a nitrene. This nitrene reacts with a C–H-bond of an adjacent organic molecule, in our case a neighboring polymer chain. As depicted in Figure 4, the nitrene exists in an equilibrium between the singlet and the triplet state, which can lead into different reaction paths. The singlet nitrene

**Table 1. Cross-Linking Behavior of Azide-Modified Polymers**

| polymer | $T_{\mathrm{Gel}}$/°C | Gel$_{\max}$/% |
|---|---|---|
| P[MMA-1%SSAz][a] | 150 | 100 |
| P[MMA-9%SSAz][a] | 130 | 100 |
| P[S-5%SSAz][a] | 130 | 100 |
| P[S-10%SSAz][a] | 120 | 100 |
| P[SBr-3%SSAz][a] | 140 | 100 |
| P[PAA-1%SSAz][b] | 170 | 95 |
| P[PAA-2%SSAz][b] | 160 | 100 |
| P[PAA-4%SSAz][b] | 150 | 100 |
| P[SSNa-5%SSAz][b] | 140 | 100 |
| P[MAA-2%SSAz][b] | 140 | 100 |
| P[DMMA-1%SSAz][b] | 150 | 97 |

[a] Azide content determined through FT-IR measurements. [b] Azide content determined through elemental analysis. $T_{\mathrm{Gel}}$ is defined as the temperature where a gel content of 90% is reached after 1 h heating. Gel$_{\max}$ is the maximum gel content reached in the experiment.

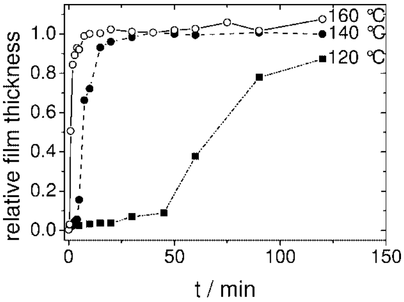


**Figure 6.** Kinetics of the gel formation of P[MMA-9%SSAz].

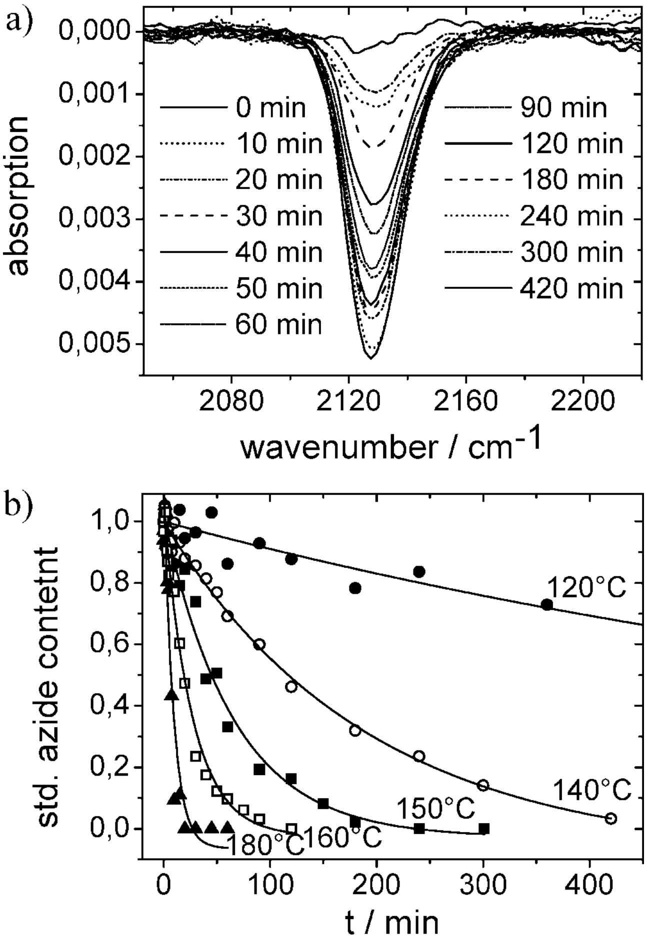


**Figure 7.** Cross-linking-studies of P[MMA-9%SSAz] thin films on surface-modified silicon-wafers. (a) FT-IR spectra of the N$-$*N*$=$N vibration band of a 100 nm thick film after varying times of heating at $T = 140$ °C. (b) Azide contents of the polymers as a function of heating time. Solid lines are fit curves according to first-order kinetics.

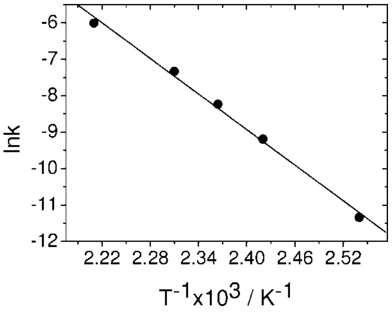


**Figure 8.** Arrhenius plot for the azide decomposition in P[MMA-9%SSAz].

can insert into the C$-$H-bond of a contacting organic molecule and forms this way a secondary sulfonamide. In contrast to this the triplet nitrene abstracts a proton, which leads to formation of a radical site on the polymer chain while at the same time a sulfonyl radical is created. These two radicals can either recombine to form the sulfonylamide to yield the same products as in the insertion case or abstract another hydrogen atom, which leads to a primary sulfonyl amide, which does then not connect two chains. In IR-experiments, a slight loss of the $SO_2$-group was also observed in our experiments. This cleavage is proposed to occur through a radical process, but the exact mechanism is not yet understood.[33]

All experiments were carried out under ambient conditions, i.e., in air. A comparison between analogous experiments in air and under argon atmosphere exhibited no differences in respect to the cross-linking (gel content) and azide decomposition behavior. Some reports in the literature mention the reactions of nitrenes with oxygen, which can result in the formation of nitro-, nitroso- and peroxo-compounds as well as some other byproducts. In other literature reports, it is stated that the absence of oxygen in the cross-linking of polyolefins with disulfonylazides is important.[33,42−44] We cannot exclude this byproduct-formation. But, nevertheless, in our case the results of experiments on the film formation in air and argon were totally indistinguishable.

In a first set of experiments we examined the required cross-linking temperature to obtain high gel contents by heating a series of polymer layers for 1 h at different temperatures between 80 and 180 °C. The gel content of the obtained thin film systems was determined from the ratio of the film thickness after heating, to the thickness after a thorough Soxhlet extraction (16 h) in a good solvent. Such an extraction procedure guarantees a complete removal of the uncrosslinked polymer chains from the film.

Figure 5 shows the cross-linking behavior of azide group containing PMMA together with a control experiment, which was performed under identical conditions, but with PMMA without azide groups. In the case of azide-modified PMMA-samples a gel content of 100% was rapidly reached, if the temperature was chosen sufficiently enough, while unmodified PMMA was completely washed off under all conditions, even after short extraction. This is a direct proof that cross-linking takes place due to the incorporated azide groups and is not caused by heat induced side reactions.

The same measurements were carried out with other azide-containing polymers again with a heating time of 1 h. The results are given in Table 1. All polymers cross-linked due to the incorporated sulfonyl azide groups and reached in most cases a 100% gel contents, even if the azide contents of the polymers was rather low. The details of the reaction depended on the amount of cross-linker as well as the nature of the polymer. Slight differences were visible between the different polymers, especially the more hydrophilic copolymers required in general

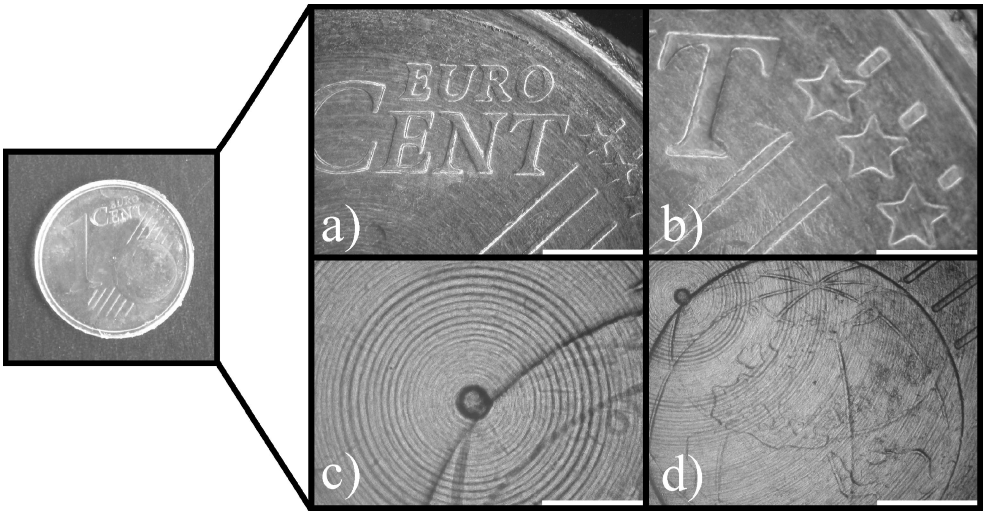


**Figure 9.** Photographs of a hot embossed polymer structure using a 1 Euro cent coin as a mask. The polymer used was PMMA-2%SSAz, the embossing conditions were $T = 170$ °C, the pressure was 3 kN applied for 10 min. Scale bars are (a and d) = 2000 $\mu$m or (b and c) = 1000 $\mu$m.

slightly higher temperatures or longer reaction-times to ensure complete cross-linking. Regardless of these small differences, these results demonstrate the versatility of the system, as so far thin film formation can be obtained with a wide spectrum of different polymers.

One important question is whether any degradation occurs during heating of the polymers. To this thermogravimetric (TGA) experiments were performed. TGA-measurements of P[MMA-SSAz] at 160 °C showed after an initial mass decrease due to the nitrogen loss during azide decay, no further mass loss even when heated to this temperature for 2 h. Control samples of the polymers without azide groups were also heated under the same conditions and investigated by NMR and GPC, where no changes in the properties were observed.

In another set of experiments, the kinetics of the cross-linking reaction was examined. To elucidate this in more detail we choose P[MMA-9%SSAz] as the standard polymer for the experiments. The polymer layers were prepared as described before and heated for different period of times at a given temperature. Again, the gel content was determined by comparing the film thickness after extraction to the film thickness after heating. Figure 6 shows the gel fraction for three different polymers. At temperatures of 140 °C or above, complete cross-linking occurred within minutes, whereas at 120 °C even after several hours still significant amount of polymers, which were not part of the infinite network could be washed out. Thus, the temperature range of the cross-linking process could be lowered by roughly 100 °C in comparison to related literature reports, where a 4 + 4 cycloaddition or benzylazides was used for the thermal cross-linking.[24,30] In particular, when polymers are chosen that are prone to thermal degradation, this is a significant advantage.

The second parameter, which is important for prediction of the cross-linking behavior of the films, is how many azide groups are actually activated during heating. Knowledge of this parameter is important as the time required to form an infinite network depends on the azide decay kinetics and the number of azide groups per polymer, which in turn depend on the azide contents and the molecular weight of the polymer. To obtain the azide decay kinetics, the contents of azide groups still intact after heating of the film for a certain period of time was determined. To this FT-IR spectra were analyzed after heating of the samples and measurement of the film thickness. Some typical spectra and the resulting decay kinetics obtained from the FT-IR investigations are depicted in Figure 7.

The rate of conversion for a first-order reaction is described as

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}] \Rightarrow \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt \qquad (1)$$

where [A] is the actual concentration of reactant A at a given reaction time.[45] By plotting the logarithm of the rate of conversion $[\mathrm{A}]/[\mathrm{A}]_0$ against time t, linear behavior was found for each temperature studied. The activation energy and the Arrhenius parameter *A* were determined by plotting the logarithm of the initial rate constant against the inverse temperature $1/T$ (Figure 8). The values for activation energy (135 kJ/mol) and *A* ($1.25 \times 10^{13}$) are in agreement with literature values for the decay of low molecular weight bissulfonylazides.[33]

Besides the generation of thin surface-attached polymer films, sulfonyl-azide-containing polymers turned out to be excellent candidates for obtaining microstructures through hot embossing. In this process, polymers are patterned with a stamp above its glass transition. At elevated temperatures, however, the patterns begin to flow and deform.[46] Due to the ability to cross-link on heating, the polymers described here, become cross-linked and microstructured simultaneously. Such a thermoset behavior can be reached even with small contents of reactive groups involved in the cross-linking process, compared to other strategies based on polymeranalogous condensation or addition reactions. In contrast to other strategies, our concept does not involve low molecular weight cross-linking agents and thus avoid problems like shrinking, bleeding of low molecular weight compounds or immiscibility.[47,48]

Exemplarily, we used an Euro cent coin as a stamp for structuring a PMMA-2%SSAz-copolymer. Hot embossing was performed at 170 °C with a power of 3 kN for 10 min leading to the structured polymer shown in Figure 9. Even fine details, such as delicate microstructures from the cent surface appear clearly in the cured polymer. More detailed experiments concerning the formation of micro- and nanostructures following this approach will be reported in a following communication.

## Conclusion

In this paper, we describe a simple and versatile thermal process for the modification of surfaces with thin films consisting of surface-attached polymer networks. To this thermosensitive sulfonyl azide groups are introduced into a polymer through copolymerization of an azide group monomer with a base comonomer. In a second step the thus obtained polymers are deposited onto a substrate through spin-coating, dip coating or other means of thin film formation. Surface-attachment and network formation occur simultaneously upon heating via azide decomposition followed by C−H-insertion with neighboring chains. As no reactions between specific functional groups are required, our approach allows to work with much lower contents of reactive groups compared to cross-linking through typical bifunctional polymeranalogous condensation or addition reactions. The described process allows to modify surfaces of many different types of materials ranging from polymers or inorganic solids such as silicon wafers provided that they had been previously coated with an arbitrary self-assembled monolayer.

Following this method, surface-attached networks with precisely tailored chemical and physical properties can be prepared in a very simple way. Variation of the cross-link density can be achieved either through changing the composition of the copolymer or blending with homopolymer carrying no sulfonyl azide groups. Thanks to the covalent attachment of the networks to the surface, the obtained surface-attached films are very robust, especially against solvent exposure.

The copolymers can be easily microstructured by hot embossing leading to formstable thermosets in a one step process. In contrast to other approaches, which use either low molecular weight cross-linkers or form networks through a cross-linking polymerization, no problems concerning miscibility or shrinkage due to the consumption of low molecular weight compounds can occur. In particular, for systems where a photochemical network formation is not possible, the described approach might represent a powerful alternative pathway for thin film formation.

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**Supporting Information Available:** Text and figures outlining the determination of copolymerization parameters, the FT-IR calibration with propylbenezenesulfonyl azide and its synthesis for obtaining the azide content, the curves of the gel content for the individual polymers, and the plots for the IR kinetic of P[MMA-9%SSAz] as well as NMR and IR spectra of low molecular weight compounds and polymers and a table of the data for molecular weight. This material is available free of charge via the Internet at http://pubs.acs.org.

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