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Surface-Initiated Polymerization on Self-Assembled Monolayers: Effect of Reaction Conditions

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Summary: Self-assembled monolayers of 4′-nitro-4-mercaptobiphenyl were modified by electron beam irradiation and diazotization to create a surface-bond asymmetric azo initiator for the surface-initiated polymerization (SIP). The effect of different reaction conditions upon the thermally and photochemical initiated SIP was investigated.

Keywords: azo initiator; decomposition; polymer brushes; self-assembled monolayers; surface-initiated polymerization

Introduction

The concept of surface-initiated polymerization (SIP) to prepare dense and well defined polymer brush systems on solids has been demonstrated for all types of polymerization[1] such as the (controlled) radical,[2-4] living cationic[5] and anionic polymerization.[6] Especially when self-assembled monolayers (SAMs) are used as initiator systems for the SIP, one can control the locus of the initiator sites and therefore prepare well-defined structured polymer brushes. Recently, we demonstrated the synthesis of patterned polymer brush layers on the micro- and nanometer scale via radical polymerization.[2] Commonly, the synthesis of polymer brushes by means of free radical polymerization is carried out by thermal decomposition of surface bond azo compounds. As surface initiator systems, either SAMs of alkyl or aryl thiols on gold or silane based SAMs on silica substrates are used. Although, highly organized SAMs of thiols on Au(111) are much easier to prepare, the thiol/Au-SAM system bears the disadvantage of desorption of the polymer brushes

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at elevated temperatures due to the relatively labile gold-sulfur bonding -especially for the thermal SIP.[7,12] Hence, alternative polymerization methods such as the surface-initiated photopolymerization (SIPP) are now discussed with increasing attention. The SIPP is a milder method for the preparation of polymer brushes because the polymerization reaction can be carried out at room temperature.[8-10]

In general, the initiators used for the photopolymerization can be divided into cleavable photoinitators and photoinitiators involving H-abstraction or electron transfer reactions.[11] Examples for the first class are e.g. benzoin ethers, phosphine oxide derivatives, peroxides and, especially on surfaces, azo compounds;[11] whereas the latter include benzophenones, benzyl compounds or thioxanthones.

In this paper we briefly outline our findings on the thermal initiated radical polymerization using azo-functionalized SAM systems, and the thermal stability of the polymer brush systems. In consequence, we then motivate the advantages of surface-initiated photopolymerization (SIPP) under different irradiation conditions with our latest results.

Results and Discussion

1) Azo Initiator System.

Azo initiator systems can be classified as symmetric and asymmetric compounds. Symmetric azo initiators bonded onto a surface decompose in two radicals of equal reactivity e.g. both capable of initiating the radical polymerization. In consequence, the polymerization proceeds as a ‘grafting from’ reaction at the interface, as well as in solution. In contrast to that, asymmetric azo initiators can be designed in such a way that upon decomposition, two radicals of different reactivities are formed. If the surface-bonded fragment is of significantly higher reactivity, only the ‘grafting from’ polymerization proceeds in the initial state. Free radical polymerization in solution can then only occur by chain transfer reactions or autopolymerization. Especially in the initial stage of free-radical surface polymerization the high local concentration of free radicals near the interface augments the impact of termination reactions by combination of free radicals. This will result in a decrease of the grafting density or broaden the molar mass distribution of grafted chains in the final polymer brush. Figure 1 show such a surface-bond asymmetric azo initiator which can be used for thermally initiated and photochemical initiated surface polymerization. This initiator decomposes into a highly reactive surface-bond biphenyl radical initiating the surface polymerization and a methylmalonodinitrile radical as the detached radical fragment. While the surface-bond biphenyl radical is highly reactive, the cleaved methylmalonodinitrile radical is not able to initiate polymerization of vinyl monomers due to resonance stabilization. Hence, only a SIP can be expected. Another advantage of the depicted aromatic azo compound is its biphenyl system. Due to the conjugation to aromatic units, this initiator has a much higher extinction coefficient than common aliphatic azo compounds. This renders the initiator as an ideal candidate for the surface initiated photopolymerization.[9]

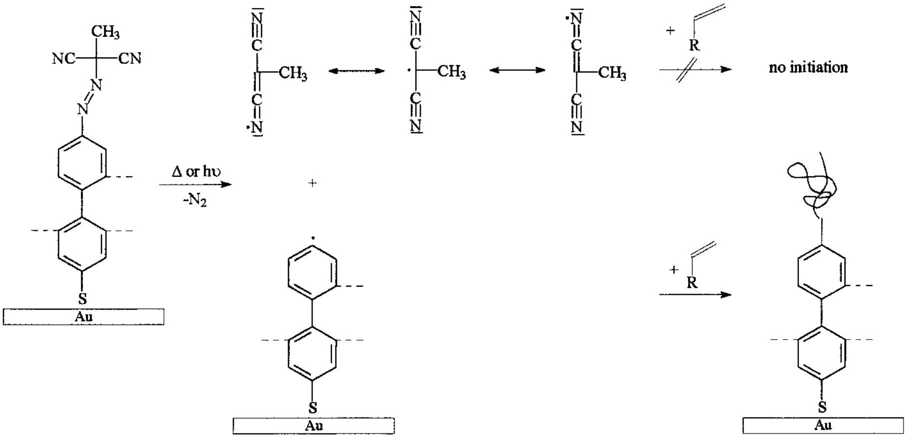

Figure 1: Surface-bond initiator SAM used for the thermal and photochemical SIP.

2) Thermal Initiated Surface Polymerization (SIP).

Polystyrene brushes were generated via thermal decomposition of a SAM of asymmetric azo initiator on a gold substrate to initiate radical surface polymerization. The substrates covered with a crosslinked SAM of 4'-azomethylmalonodinitril-1,1'-biphenyl-4-thiol were immersed in a mixture of styrene and toluene (styrene:toluene 50:50 mol%) at 80 °C. After the polymerization, the substrate was cleaned in toluene by soxhlet extraction (~ 230 extraction cycles). The temperature of the solvent in the extractor was about 85-90 °C. Before and after soxhlet extraction the thicknesses of polymer brush layers in the collapsed state (in air) were measured by null-ellipsometry (Figure 2). Homogeneity of all prepared polymer brush layers were additionally checked by scanning probe microscopy (Nanoscope IIa; tapping mode; areas from 100 to 1 μm^2).

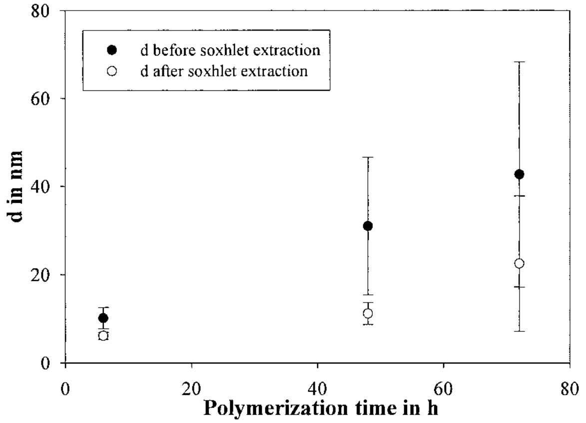

Figure 2: Comparison of the polymer layer thickness d before and after soxhlet extraction (layer thickness was measured by ellipsometry; values are averaged values calculated from seven measurements of individual spots on each sample; error bars reflect the standard deviation).

Comparing the polymer layer thickness before and after the cleaning process with hot toluene as a good solvent for polystyrene, a significant decrease of about 50 % in the total layer thickness were observed. It is noteworthy, that a pure SAM of alkyl or aryl thiols on Au(111) would completely desorb under such conditions.[12] The decrease in the brush layer thickness indicates a decrease of the total grafting density by desorption of polymer chains (the layer thickness, L, scales with the grafting density, σ, as: $L \sim \sigma^{1/3}$). It is most likely that also during the chain growth at 80 °C significant desorption of chains occurs. Thus, the 'final' layer thickness after the polymerization is the result of chain growth by SIP and the desorption process. These observations call for milder reaction conditions for the synthesis of polymer brushes such as a photochemical initiated polymerization as well as milder conditions for the work-up procedure.

3) Photochemical Initiated Surface Polymerization (SIPP).

We investigated the SIPP of styrene using different wavelengths for the decomposition of the azo-SAM ($\lambda_{max} = 300$ nm and $\lambda_{max} = 350$ nm). Figure 3 shows the increase of the polystyrene layer thickness with the irradiation time ($\lambda_{max} = 300$ nm, quartz glass tubes, continuous irradiation, T = r.t.).

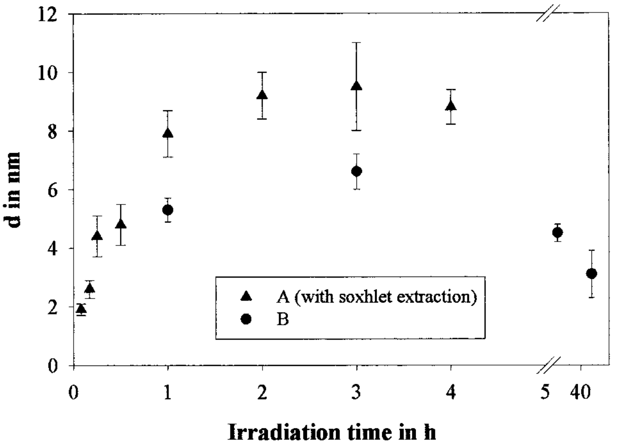

Figure 3: Dependence of the polymer layer thickness on the irradiation time at $\lambda_{max} = 300$ nm; series of individually prepared samples cleaned by (▲) soxhlet extraction, by (●) exhaustive washing with toluene[13] (layer thickness was measured by AFM; values are averaged values calculated from three measurements of individual spots on each sample; error bars reflect the standard deviation).

As depicted in Figure 3, the polystyrene brush layer thickness constantly increases within the first 2 h of irradiation. Longer irradiation/reaction time, however, does not result in a further increase of the brush layer thickness. Around 3 h a stagnation was observed and longer irradiation at $\lambda_{max} = 300$ nm causes a decrease of the brush thickness. The maximum thickness of approximately 10 nm was obtained after 2-3 h. This can be explained by the simultaneous processes of SIP, creating the polystyrene brush, and significant photochemical decomposition of polystyrene brushes upon irradiation at 300 nm. As polystyrene absorbs wavelengths lower than $\lambda = 280$ nm, the polymer is degraded by disproportion and cross-linking.[11] Steady irradiation causes a broadening and a shift of the absorption spectrum of polystyrene to higher wavelengths and therefore an increase of the decomposition of the polymer. Considering the spectral distribution of the irradiation source ($\lambda_{max} = 300$ nm) of the Rayonet Photochemical Chamber Reactor (Figure 4) and that quartz glass tubes are permeable for wavelengths below $\lambda = 300$ nm, SIP and degradation of polystyrene takes place. At irradiation times longer than 3 h the decomposition of the polymer overbalances the polymer brush growing and the layer thickness decreases. Duran glass tubes with a cut-off for UV light with $\lambda < 300$ nm should prevent initial degradation of the polystyrene brush layer (Figure 4).

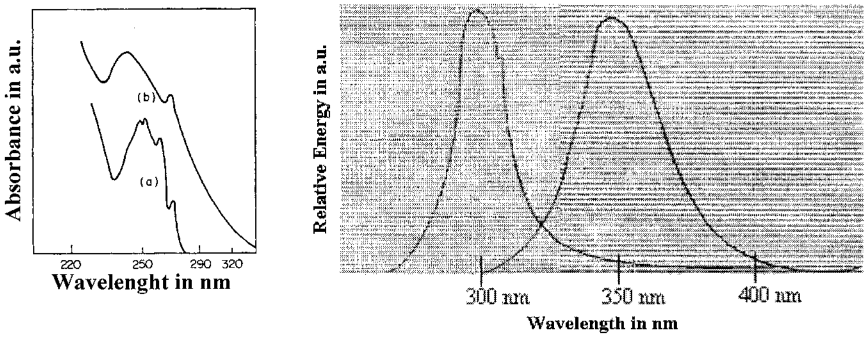

Figure 4: *left*: UV absorption spectra of (a) undegraded, (b) degraded polystyrene; *right:* spectral distribution of two UV-light sources (λ_{max} = 300 nm and λ_{max} = 350 nm) of the Rayonet Photochemical Chamber Reactor used in this study.

We irradiated the initiator monolayers with light of a spectral distribution between 300 nm and 400 nm (λ_{max} = 350 nm) for different irradiation times (Figure 5). Comparing Figure 3 and Figure 5, significantly higher total layer thicknesses were obtained. During the first 6 h the polymer layer thickness increases linear. At longer irradiation times the increase of the layer thickness levels off. Elimination of the competitive polymer degradation at $\lambda < 280$ nm the layer thickness can be nicely controlled by means of the irradiation time. Furthermore, the total layer thicknesses are significantly higher at any reaction/irradiation time.

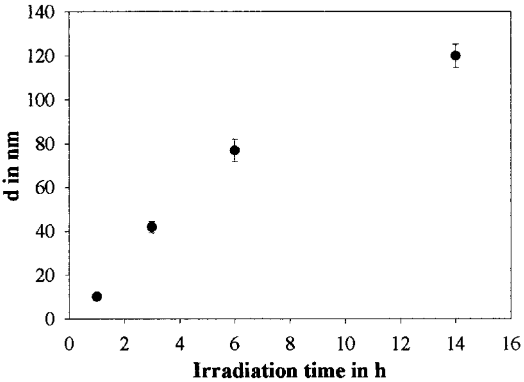

Figure 5: Dependence of the polymer layer thickness on the irradiation time at λ_{max} = 350 nm; (●) series of individually prepared samples cleaned by exhaustive washing with toluene (layer thickness was measured by AFM; values are averaged values calculated from six measurements of individual spots on each sample; error bars reflect the standard deviation).

Comparing these results with SIPP experiments performed by *Rühe et al.*,[14] the different photochemical behavior of aliphatic and aromatic compounds is evident. Although *Rühe* and coworkers applied wavelengths over 360 nm the polymer layer is about 30 nm after a polymerization time of 4 h. This reveals that the used aliphatic azo initiator has a much lower extinction coefficient and therefore is not as efficient in photopolymerization as the aromatic derivatives. In another account, *Rühe et al.* used a similar surface-bonded aryl azo-initiator.[10] Indeed, in these studies they observed a similar brush growth for the photochemical initiated radical polymerization on surfaces.

Conclusion

It has been shown that at elevated temperatures, desorption of polymer brushes grown by SIP on SAM of thiols on Au(111) takes place. Presumably, the detachment point is the Au/S bonding. Photopolymerization carried out at room temperature circumvents this problem and is a better alternative to synthesize dense, homogeneous and significantly thicker polymer brushes by SIP. Additionally, the dependence of the degradation of polystyrene brushes on the used wavelength during photopolymerization was found. After optimization of the reaction parameters a controlled synthesis of polymer brushes via photochemical initiated surface polymerization was obtained.

Acknowledgement

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