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Photoinduced Polymerization from Dimethylamino-Terminated Self-Assembled Monolayers on Gold

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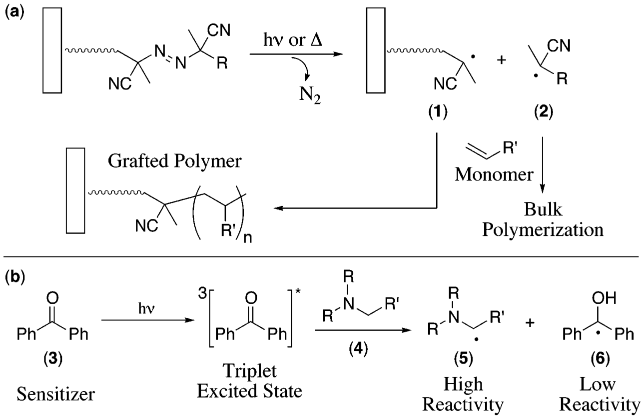
The synthesis of functional organic thin films with well-defined architectures is an important goal in contemporary polymer chemistry. In particular, polymer brushes offer the ability to control the lateral resolution and film thickness on the micron and nanometer scales. Polymer chains that are grafted or adsorbed to an interface are termed "polymer brushes" when the grafting density is sufficient to cause the chains to stretch away from the interface.[1,2] Such films may respond to their environment and will play an important role in the design of novel smart materials for a variety of technologies including biocompatible surfaces,[3] tissue engineering,[4] controlled adhesion and wetting,[5] and microfluidic[6] or nanofluidic[7] devices.

New methodologies for the synthesis of polymer brushes are continuously under development, and a variety of initiating mechanisms have been used.[8] However, photochemical initiators offer distinct advantages over thermal initiation,[2,9,10] particularly when the substrate consists of alkylthiolate self-assembled monolayers (SAMs) on gold, since these monolayers are not stable at the elevated temperatures where thermal polymerizations typically occur. Furthermore, photochemical initiation is usually more rapid than thermal and also allows for the lithographic patterning of planar substrates.[9]

The most widely used photoinitiators in polymer brush synthesis have been derivatives of 2,2′-azobis(isobutyronitrile) (AIBN).[11] However, azo initiators like AIBN have a relatively low absorbency and long half-life,[12] thus necessitating long curing times. Furthermore, activation of AIBN produces two radicals, only one of which is tethered to the surface. As illustrated in Scheme 1a, the untethered radical **2** diffuses into solution and initiates polymerization in the bulk. This bulk polymer then intercalates into the grafted brush and requires a Soxhlet extraction for complete removal. Alternatively, atom transfer radical polymerization (ATRP)[13] and reversible addition−fragmentation chain transfer (RAFT)[14] polymerization can be used at room temperature to eliminate most of the bulk polymer in solution. However, brush synthesis by these techniques generally yields films less than 40 nm in thickness and is much slower than photoinitiated free radical polymerization.

We examined photosensitizing strategies in order to maximize the rate of film growth, while reducing the amount of residual polymer in the bulk solution. In particular, triplet photosensitizers initiate polymerizations by abstracting hydrogen atoms from 3° amines.[15] As Scheme 1b illustrates, benzophenone (**3**) absorbs UV light and forms a triplet state that abstracts a hydrogen from amine (**4**). The resulting radical (**5**) is an efficient polymer initiator, whereas the ketyl radical (**6**) is less reactive and may condense to form benzopinacole derivatives.

Scheme 1. (a) Grafting-From Synthesis of Polymer Brushes with 2,2-Azobis(isobutyronitrile) (AIBN) Type Initiators; (b) Photoinitiation with Triplet Sensitizers and 3° Amines



We designed a series of dimethylamino-terminated thiols and disulfides in order to synthesize polymer brushes from gold substrates. Our initial SAMs were composed of compound **7**, which formed densely packed and highly crystalline monolayers. The film thickness by ellipsometry was 2.1 nm, which is very close to the calculated length of the molecule in the gas phase (Table 1). Since compound **7** was difficult to synthesize and purify, we synthesized amino-initiator **8** and compound **9** as a control. The formation of the SAMs (**7**−**9**) was confirmed by water contact angles, which are consistent with the proposed terminal groups, as are the reflection−absorption infrared (RAIR) spectra, the X-ray photoelectron spectroscopy (XPS) spectra, and the ellipsometric thickness (Table 1).

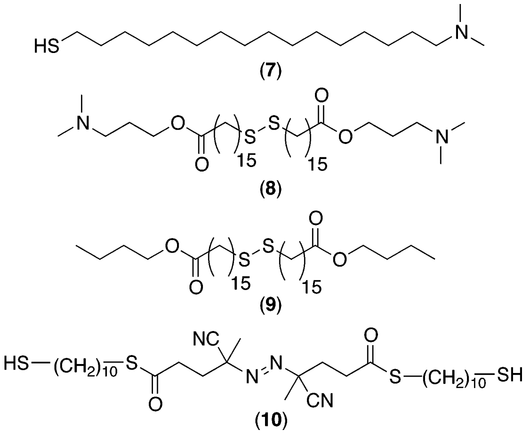


Figure 1. Structures of the self-assembled monolayer (SAM) initiators.

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Table 1. Water Contact Angles and the Theoretical and Observed Thickness of the Self-Assembled Monolayers (SAMs)[a]

compd	static water contact angle of SAM (deg)	thickness obsd (nm)	thickness calcd (nm)
7	45 ± 1	2.1 ± 0.1	2.28
8	50 ± 1	2.2 ± 0.1	2.84
9	78 ± 1	2.1 ± 0.2	2.71

[a] Calculated thicknesses were performed with HyperChem v. 6.03 (Hypercube, Inc.) using a semiempirical PM3 model and the Polak−Ribiere optimization algorithm for isolated molecules in vacuo.

Polymerization of styrene was carried out with a SAM of **7** and 15 h of irradiation at room temperature, followed by a Soxhlet extraction with tetrahydrofuran (THF). We clearly observed PS by RAIRS along with a static water contact angle that is consistent with PS (88°). Ellipsometry yielded an optical thickness of 140 ± 0.7 nm; PS was also found in the bulk solution, which is expected under these conditions as styrene can autopolymerize.[16,17]

For control experiments we repeated the polymerization using clean gold substrates, as well as octadecanethiolate (ODT) SAMs, and did not observe grafted PS after cleaning. Thus, the S−Au bond is stable and does not participate in chain transfer, nor does the polymer adsorb strongly to gold. In addition, we repeated the experiments with SAMs of **7** in the absence of benzophenone. To our surprise, PS was grafted to the substrates, and the thickness increased to 202 ± 3 nm. Thus, the films were actually thicker in the absence of the photosensitizer. Previously, benzophenone-derivatized SAMs had been used as photosensitizers to graft polymer to solid surfaces;[18] therefore, it is likely that the activated benzophenone in solution is inhibiting initiation and propogation by radical termination.

We also explored SAMs of **8** and **9**. As expected, the alkyl-terminated SAM of **9** did not lead to the formation of grafted PS: however, compound **8** yielded a PS film of 273 ± 1 nm after only 8 h of irradiation. Clearly, the dimethylamino group is necessary for polymerization, and the internal ester does not play an active role. Furthermore, the rapid growth of these films is surprising, especially in the absence of a photosensitizer.

We also examined the effect of the reaction time on the film thickness for SAMs of **8**. As illustrated in Figure 2a, the film thickness for the polymerization of styrene increases from 9.6 ± 0.1 nm after 1 h to 103 ± 3 nm after 5 h and 395 ± 1 nm after 11 h before terminating at 427 ± 1 nm at 16 h. It is interesting to compare the rate of PS growth from SAMs of **8** to that of similar grafting-from (GF) experiments with an AIBN type SAM from initiator **10** (Figure 2b).[19] Both initiators **8** and **10** exhibit three growth phases as is typical for GF brush films of PS: This includes an initial slow growth period followed by a rapid growth phase, which ends in termination. However, the growth from SAMs of **8** was more rapid and terminated with a thickness that was more than twice that for initiator **10**. To our knowledge this is the most rapid film growth reported to date for PS brushes.

The rapid growth kinetics suggest that we are not simply grafting chains that were preformed in the bulk by autopolymerization. Importantly, grafting-to (GT) mechanisms typically lead to PS brush thicknesses of less than 10 nm due to polymer diffusion limits;[20] therefore, it is highly unlikely that this reaction proceeds via a GT mechanism. We propose two alternative GF mechanisms for the surface initiation: First, active chains from the bulk solution may participate in chain transfer and abstract hydrogen atoms from the surface bound dimethylamino groups. Thus, the grafted polymer is a result of surface bound radicals, and the growth kinetics exhibit a (GF) profile. However, this mechanism would likely suffer from the same diffusion limitations as GT because it would be difficult for the reactive polymer chains to diffuse to the surface bound amino groups. Alternatively, the monomer could absorb a photon and act as a photosensitizer to activate the amino group by electron transfer or hydrogen abstraction. Indeed, charge-transfer complexes have been observed between monomers and tertiary amines.[21] Furthermore, Yang has suggested that photoexcited PS can abstract hydrogen atoms from low-density polyethylene (LDPE) to initiate a GF polymerization of styrene.[17]

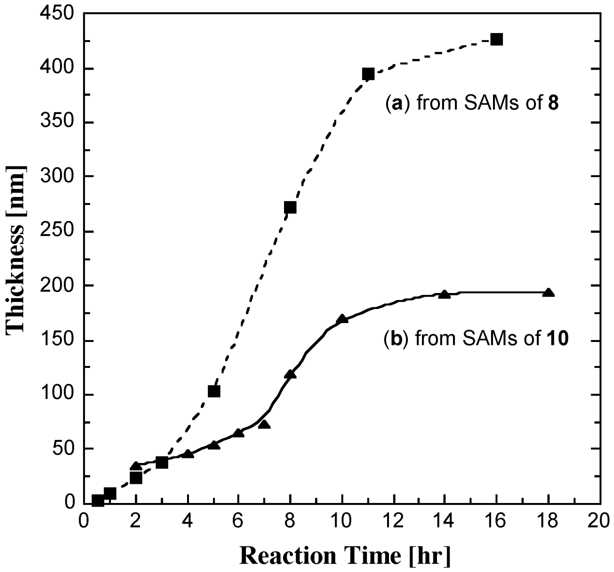

Figure 2. Growth kinetics for a polystyrene brush from self-assembled monolayers (SAMs) of (a) amino initiator **8** and (b) initiator **10** based on 2,2-azobis(isobutyronitrile) (AIBN).

To gain more insight into the mechanism, we examined the number-average molecular weight (M_n) of the polymers. There is evidence to suggest that the M_n for grafted polymers is similar to that in the bulk solution for free radical polymerizations from planar substrates.[10,22] It is also possible to increase the amount of polymer in solution and to decrease the M_n by adding air to the system.[16] This occurs because oxygen accelerates the autoinitiation of styrene, while simultaneously inhibiting the chain growth (i.e., M_n). After 3 h irradiation in air we observed a film thickness of 38 nm and a M_n of 43 790 Da in the bulk; however, under nitrogen the M_n increased more than 4-fold to 191 900 Da, while the thickness remained the same. After 5 h irradiation the M_n and thickness in air are 39 160 Da and 86 nm, respectively; this compares to 210 980 Da and 103 nm under nitrogen. Furthermore, the M_n and % conversion for polymerizations with the initiator SAMs are quite similar to those of control experiments with clean gold substrates; this suggests that the SAMs have little effect on the bulk polymerization. In all cases the polydispersity ranged from 1.3 to 1.48 and are typical for PS under these conditions.[23] Finally, the calculated grafting densities (D_s) in air are 0.55 and 1.4 chains/nm^2 for 3 and 5 h, respectively. Interestingly, the D_s in air is nearly 5 times greater than that under nitrogen, which suggests that oxygen is accelerating the initiation at the surface. Indeed, Sato has examined the rate enhancement observed for PMMA due to the addition of oxygen and amines.[21] He proposed a charge-transfer mechanism for the initiation step, which we favor over an alternative chain-transfer mechanism.

To further explore the utility of the diamino SAMs, we synthesized poly(methyl methacrylate) (PMMA) brushes. In particular, a solution polymerization in toluene with a SAM of **8** yielded a PMMA brush of 56 ± 0.4 and 675 ± 8 nm after 2 and 15 h, respectively. Furthermore, addition of benzophenone reduced the film thickness by more than half to 250 ± 3 nm at 15 h. Thus, dimethylamino-terminated SAMs provide very efficient initiating systems for the synthesis PS and PMMA brushes. In addition, benzophenone decreased the rate of film growth, while the addition of oxygen increased D_s significantly.

We observed very rapid film growth for PS brushes, which strongly suggests a GF mechanism. While the initiation step remains elusive, experiments are in progress to explore this chemistry in more detail. In particular, we will thoroughly investigate the role of oxygen and increase the scale of the reaction to acquire the M_n for tethered polymer in addition to that in the bulk. These results suggest that dialkylamino SAMs are excellent initiating systems for the synthesis of grafted polymers. Thus, it is possible that other amine-modified substrates will perform as well, such as silicon, glass, or even organic copolymers. New synthetic methodologies such as this will play an important role in emerging fields that require well-defined polymer films in the nanometer regime.

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Supporting Information Available: Detailed description of synthesis and experimental procedures and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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