

Rewritable Materials

Rewritable Polymer Brush Micropatterns Grafted by Triazolinedione Click Chemistry

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Abstract: Triazolinedione (TAD) click reactions were combined with microcontact chemistry to print, erase, and reprint polymer brushes on surfaces. By patterning substrates with a TAD-tagged atom-transfer radical polymerization initiator (ATRP-TAD) and subsequent surface initiated ATRP, it was possible to graft micropatterned polymer brushes from both alkene- and indole-functionalized substrates. As a result of the dynamic nature of the Alder–ene adduct of TAD and indole at elevated temperatures, the polymer pattern could be erased while the regenerated indole substrate could be reused to print new patterns. To demonstrate the robustness of the methodology, the write–erase cycle was repeated four times.

The fabrication of micro- and nanostructured polymer substrates is a key focus of materials science, leading to devices with potential applications in information storage,^[1] electronic devices,^[2,3] biosensing, and antifouling coatings.^[4-11] In this context, polymer brushes grown by the "grafting-from" approach are especially attractive, because an excellent control of film thickness is given and high grafting densities are accessible. In principle any chemical functional group can be incorporated into the brushes, as a wide variety of monomers is available. To date, many different polymer materials have been used in combination with various lithography techniques to tailor surface properties, yielding substrates with enhanced functions.^[12-15] One type of soft lithography that has been frequently used for the generation of patterned self-assembled monolayers (SAMs) is microcontact printing (μCP) .^[16,17] In μCP , a SAM is patterned by means of a selective transfer of an ink from a patterned stamp to a substrate exclusively in the area of contact. µCP features a set of advantageous properties such as low cost and low consumption of material, large and fast area patterning, high

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506361. pattern resolution, high versatility, and preparative ease and simplicity. For example, µCP has been used to form patterned SAMs of polymerization initiators on gold surfaces employing thiols as anchoring moieties. Subsequent surface initiated polymerization results in microstructured polymer brushes.^[18,19] Microcontact chemistry (µCC) is a variation of µCP in which a substrate, coated with a reactive layer, is brought into close conformal contact with an elastomeric stamp, which is soaked with an ink containing complementary reactive groups, thus leading to surface functionalization by a chemical reaction exclusively in the area of contact. Click reactions in particular were found to be versatile for surface functionalization via $\mu CC.^{[20,21]}$ While most of the examples cited above aim for a robust and irreversible surface functionalization, only very few reactions offer stable (that is, covalent) yet dynamic grafting with switchable surface properties. One example is the elegant photoclick system reported by Popik and Arumugam, which works very well for small molecules.^[22] Barner-Kowollik and co-workers used the reversible nature of Diels-Alder reactions between reversible addition fragmentation transfer (RAFT) agents and cyclopentadienyl moieties to graft polymer brushes onto silicon substrates in a non-patterned fashion to detach them at elevated temperatures and thus switch surface properties owing to reversible grafting.^[23]

We recently employed Diels–Alder and Alder–ene reactions of various reactive triazolinediones (TAD) with a range of dienes and alkenes to produce block copolymers, crosslinked plant-oil-based materials, and also covalently linked layer-by-layer assemblies on surfaces (Scheme 1 a).^[24–26] These TAD click reactions proceed at room temperature with high reaction rates and are often complete within seconds without the need for a catalyst, irradiation, or other external stimuli. Moreover, if an indole is used instead of a simple alkene, reversibility of the Alder–ene adduct is



Scheme 1. a) The TAD click reaction with an indole, which is reversible at elevated temperatures. b) Example of a transclick reaction: after the TAD-indole adduct is cleaved, the released TAD is captured by a diene.

observed at elevated temperatures, typically above 120°C. This reversibility could be exploited in so-called transclick reactions^[25] (Scheme 1 b), in analogy with a transesterification, yielding reversible polymer conjugation and dynamic cross-links.

Herein we report on writing, erasing, and rewriting polymer brush micropatterns on the same surface by making use of reversible TAD click chemistry (Figure 1). The use of TAD chemistry in combination with μ CC enables efficient surface patterning within a few minutes and offers, to our knowledge for the first time, the possibility to generate rewritable substrates by grafting polymers in any desired micropattern and with any desired functional group. In a first step, the irreversible patterning of a TAD-bearing initiator for atom transfer radical polymerization (ATRP-TAD) on alkene-modified substrates is shown. Subsequent surfaceinduced ATRP (SI-ATRP) affords substrates functionalized with micropatterned polymethylacrylate (PMA) brushes.

To this end, we used both glass- and silicon-supported 10undecenyl trichlorosilane SAMs as reactive substrates. These surfaces were brought into conformal contact with a PDMS stamp that was soaked with a 50 mM solution of ATRP-TAD in acetonitrile. After contacting stamp and substrate for 10 min, the stamp was lifted off and the surfaces cleaned by rinsing with acetone, dichloromethane (DCM), and subsequent sonication. The success of the TAD reaction and the micropatterned immobilization of ATRP-TAD via µCC were verified by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS; see the Supporting Information, Figures S1 and S3). The XPS spectrum shows a pronounced N1s signal (green line in Figure S3), indicating that ATRP-TAD is immobilized on the alkene monolayer. Fragments of the ATRP-TAD could also be detected in the 2D ToF-SIMS images, which mirror the pattern of the stamp. Figure 2 shows an optical microscopy image and AFM and XPS data of ATRP-TAD-functionalized substrates after SI-ATRP using methyl acrylate as the monomer.^[27] A general procedure for the preparation of polymer brushes can be found in the Supporting Information. Optical microscopy and AFM imaging provide evidence of a high edge resolution as well as the growth of polymer brushes of up to around 100 nm (Figure 2a–c). The C1s peak in the XPS spectrum shows characteristic shoulders for oxidized carbons, which proves the formation of a PMA layer (Figure 2d).

In a second step, we prepared rewritable surfaces based on the reversible reaction of TAD and indole. 10-undecenyl trichlorosilane SAMs were used to synthesize indole functionalized substrates by reacting these reactive SAMs with a thiol functionalized indole derivative via thiol-ene click chemistry (Figure 1). The covalent immobilization of indole was confirmed by XPS, contact angle goniometry, and water condensation experiments (Supporting Information, Figures S2 and S3). High edge resolutions were observed after printing times of only 5 min from a 50 mM solution of ATRP-TAD in DMSO. Figure 3 a shows ToF-SIMS analyses in which ATRP-TAD was patterned in 5 µm stripes that are spaced by 10 µm. Characteristic secondary ions of the ATRP-TAD reproduce well the chemical composition of the initiator. By immersing these substrates into a 1M solution of 2,4-hexadien-1-ol in DMF at 150°C for 1 h (procedure 1), the transclick reaction resulted in the detachment of ATRP-TAD and thus the regeneration of the surface bound indole groups. After performing the transclick reaction, the substrates were subjected to ToF-SIMS measurements again. This time, no fragments corresponding to ATRP-TAD could be found, as exemplified by the absence of the bromide signal (Figure 3b), clearly showing the dynamic nature of TAD-indole adducts on surfaces.

Remarkably, a reprint of ATRP-TAD in 10 μ m dots spaced by 5 μ m on the same substrates gave rise to the expected surface pattern without any defects, as verified by ToF-SIMS (Figure 3c). Thus, a first confirmation for the application of TAD click and transclick chemistry for rewritable surfaces has been given.

Once the dynamic nature of the TAD-indole adducts on the surface was confirmed with the low-molecular-weight ATRP-TAD, these substrates were subjected to SI-ATRP,



Figure 1. The functionalization of alkene-modified substrates by TAD click chemistry and generation of rewritable surfaces employing the transclick approach using either 2,4-hexadien-1-ol (procedure 1) or α -phellandrene (procedure 2).





Figure 2. PMA brushes grown from a 10-undecenyl trichlorosilane SAM patterned with ATRP-TAD in 10 µm stripes spaced by 5 µm: a) optical microscopy image (50-fold magnification), b) AFM 3D image, c) AFM height profile, and d) C1s signal of XPS data from PMA brushes.

again using methyl acrylate as the monomer.^[27] The outcome of the polymerization was measured with AFM and infrared spectroscopy. Along with the PMA homopolymer, 1 mol% green fluorescent nitrobenzoxadiazole acrylate (NBDA) was copolymerized into the PMA brushes at 75 °C for 3.5 h to monitor copolymer brush growth, erasing and rewriting by fluorescence microscopy. Figure 4a shows AFM and fluores-



Figure 3. ToF-SIMS data of ATRP-TAD printed in a) 5 μ m stripes spaced by 10 μ m, b) regenerated indole surface after transclick, where no bromide is detectable, and c) reprinted ATRP-TAD in 10 μ m dots spaced by 5 μ m.

cence microscopy images of a substrate functionalized with PMA-NBDA copolymer brushes of approximately 10 nm height, patterned in 10 µm stripes spaced by 5 µm. If the resulting substrates were subjected to the same conditions as the non-polymerized surfaces, that is, immersion in 1M solution of 2,4-hexadien-1-ol in DMF at 150 °C, reaction times of up to 5 h were necessary to remove all polymer brushes (procedure 1, Figure 1; Supporting Information, Figure S6). Therefore, procedure 2 was developed in which the substrates were immersed in α -phellandrene, a more potent transclick reagent, at 150°C for 45 min (procedure 2, Figure 1). Finally, AFM and FTIR spectroscopy (Supporting Information, Figures S6 and S7) suggest that detached PMA adheres to the surfaces to a small extent, which is probably due to non-specific physisorption. Thus, the surfaces were cleaned

by careful wiping with a tissue and sonication in DCM to remove the residual polymeric material as verified by AFM, IR spectroscopy, and fluorescence microscopy (Supporting Information, Figures S6, S7, and S9e).

The regenerated indole substrates were used to implement new patterns following transclick procedure 2. Surfaces were rewritten up to three times while no significant defects or reduced brush quality were observed. AFM and fluorescence microscopy data, verifying the high quality large area patterns of rewritten PMA-NBDA copolymer brushes are shown in Figure 4 and the Supporting Information, Figure S9.

In summary, we showed that the TAD click reaction is a highly efficient reaction for the reliable patterning of surfaces with ATRP initiators and polymer brushes, grown by the grafting-from approach. It was possible to immobilize initiators in a permanent manner, and furthermore the reversibility of the TAD-indole Alder–ene adduct can be exploited to generate rewritable substrates with dynamic covalent bonds. Thus, we were able to write and erase micropatterned polymer nanofilms using chemoselective grafting and degrafting reactions. These dynamic substrates have the potential to be developed to rewritable devices in materials science applications.

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Figure 4. Four consecutive write and erase cycles of polymer brushes visualized by AFM with corresponding height profile (left and middle column) and fluorescence microscopy imaging (right column, fluorescence microscopy images at 50-fold magnification). a) PMA-NBDA copolymer brushes patterned in 10 μ m stripes spaced by 5 μ m, b) rewritten PMA-NBDA copolymer brushes on the same surface patterned in 5 μ m stripes spaced by 20 μ m, c) repeated rewriting of PMA-NBDA copolymer brushes in 10 μ m dots spaced by 5 μ m, and d) subsequent rewriting of PMA-NBDA copolymer brushes in 5 μ m stripes with spacing of 25 μ m.

Keywords: click chemistry · polymer brushes · rewritable materials · soft lithography · surface chemistry

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