Graft Polycondensation

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Grafting of Polyfluorene by Surface-Initiated Suzuki Polycondensation**

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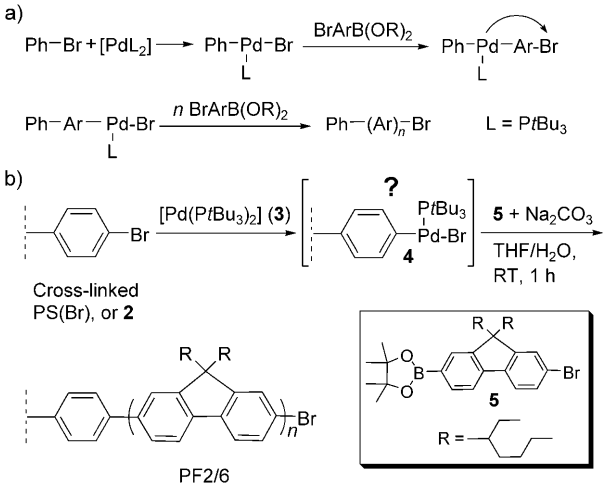
The use of conjugated polymers (CPs) in integrated circuits, solar cells, light emitting diodes, or sensors often requires their covalent fixation and patterning on various surfaces.[1] CPs can be grafted to functionalized surfaces by (electro)-chemical cross-linking,[2] however, it is difficult to control a structural order within the cross-linked films. The attachment of CP chains to substrates by their end-points to form polymer brushes would be an interesting alternative, possibly helping charge injection and charge transport processes that are crucial for many devices.[1b] A "polymerization onto" procedure consisting of a Yamamoto step-growth polycondensation combined with a grafting of in situ growing polyfluorene molecules onto properly functionalized polymer supports was recently developed by Carter et al.[3] According to this approach, however, only thin grafted layers are forming even in hard reaction conditions and a predominant quantity of the monomer forms ungrafted polymers. The surface-initiated polymerization (SIP, or "grafting-from") technique usually results in significantly thicker grafted films and can be easily applied for patterning of polymers. The SIP concept has been implemented for the grafting of various nonconjugated polymers obtainable by chain-growth polyadditions.[4] However, examples of SIP of CPs are scarce owing to the intrinsic obstacles of the step-growth route to such polymers.[5]

Nowadays, chain-growth cross-coupling polycondensations, such as nickel-catalyzed Kumada polycondensation, have become powerful tools in synthesis of well-defined polythiophenes, polyfluorenes, and some block copolymers.[6] Recently, taking advantage of the chain-growth mechanism of Kumada polycondensation, we developed SIP of regioregular poly(3-hexylthiophenes) from cross-linked poly(4-bromostyrene) (PS(Br)).[7] On the other hand, palladium-catalyzed Suzuki-coupling polycondensation of aryl halides with organoboron reagents is another remarkably efficient, versatile, route to conjugated polymers which is tolerant to various functional groups and solvents.[8] In the classical reaction, the Suzuki polycondensation is catalyzed by $[Pd(PPh_3)_4]$ or similar complexes and involves the step-growth mechanism.[8]

Recently, Yokozawa et al. reported the chain-growth Suzuki polycondensation of AB-type[8] aromatic monomers[9] mediated by an unusual three-coordinate complex $[(t\mathrm{Bu}_3\mathrm{P})\mathrm{Pd}(\mathrm{Ph})\mathrm{Br}]$ (**1**) as the catalyst (Scheme 1a).[10] It is



Scheme 1. a) Chain-growth Suzuki polycondensation and b) surface-initiated grafting of poly[9,9-bis(2-ethylhexyl)fluorene].

believed that the observed chain-growth mechanism is due a highly reactive coordination-unsaturated $\{(t\mathrm{Bu}_3\mathrm{P})\mathrm{Pd}^0\}$ catalytic intermediates, which make an intramolecular oxidative addition a more favorable pathway than an alternative intermolecular transfer.[11] It was shown that the polycondensation proceeds from the aromatic moiety derived from the catalyst and affords well-defined polyfluorenes with narrow polydispersity and controlled molecular weight (MW).[9] However, utilization of this process in the preparation of complex architectures of conjugated polymers, including surface-grafted polymers, has not been demonstrated to date.

Herein, we report the first surface-initiated and site-specific palladium-catalyzed Suzuki polycondensation to graft and pattern semiconducting and fluorescent poly[9,9-bis(2-ethylhexyl)fluorine] (PF2/6). Using our method, the grafting of PF2/6 can be successfully performed on surface-immobilized PS(Br) films, as well as on monolayers of small-molecule initiators and (optionally) on patterned initiators (Scheme 1b). In contrast to the reported "polymerization onto" methods,[3,6] our grafting process develops selectively from the surface and no detectable amounts of polymer are formed in the solution. Furthermore, the polymerization is fast even at room temperature and results in grafted PF2/6 films[12] with thicknesses up to 100 nm.

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[2-(4-bromophenyl)ethyl]chlorodimethylsilane (**2**), and lightly cross-linked PS(Br) films were used in our experiments as precursors of surface-bound initiators because of their structural similarity to bromobenzene, previously used as the precursor for the preparation of the initiator for the chain-growth polymerization (Scheme 1).[9] To prepare initiating layers, the silane **2** was deposited from the gas phase onto silicon wafers or glass slides (Supporting Information, S1-3). Alternatively, thin (from 0.5 to 10 nm) PS(Br) films were developed on these substrates which had been precoated with 1 nm thick poly(glycidyl methacrylate) (PGMA) films as an adhesion promoter. The substrates were cross-linked by irradiation with UV light, this covalently binds the PS(Br) to the PGMA making the PS(Br) insoluble. Substrates thus modified were allowed to react with $[Pd(PtBu_3)_2]$ (**3**), in toluene at 70 °C. Careful washing with copious amounts of toluene and THF removed any unbound **3**. As a result of palladium uptake, the procedure leads to an increase in the film thickness upon activation. The increase is 1–2 nm for a 1 nm thick PS(Br) film or monolayer of **2**, and approximately 10 nm for 10 nm thick PS(Br) anchoring layers. X-ray photoelectron spectroscopy (XPS) confirms a high-yield loading of palladium upon the activation of 5 nm thick PS(Br) film ([C]/[Pd] atomic ratio ca. 11.9:1 for **4** is close to the [C]/[Br] ratio of ca. 10.6:1 found for the initial PS(Br) film (Supporting Information, S4-7)). An exact structure of the "as-forming" surface-bound initiator **4** was not possible to deduce from the XPS data because of low stability of **4** under the measurement conditions. Tentatively, we propose the structure for the surface-bound initiator **4**, as shown in Scheme 1 b, by analogy with Hartwig's adduct **1**,[10] however, more investigations are necessary to elucidate the initiator structure.

To perform the surface-initiated polymerization, the substrates with freshly prepared initiator layers were placed vertically into a reactor containing 7-bromo-9,9-bis(2-ethylhexyl)-9*H*-fluoren-2-ylboric acid ester (**5**) dissolved in degassed mixture of THF and aqueous sodium carbonate solution. The grafting experiments were conducted at room temperature by stirring, typically, for 1–3 h. The technical parameters were found to be very important for successful grafting. The highest thicknesses of grafted PF2/6 films are achievable at a gentle stirring that provided a sufficient diffusion of reagents, but avoided an undesired contamination of substrates by droplets of sodium carbonate solution. No grafting of PF2/6 occurs in those parts of the substrates which appeared in a direct contact with water (bottom) phase of a biphase reaction mixture, possibly because of etching of the silicon. In optimal conditions the procedure results in uniform and smooth PF2/6 films with the thickness up to 50 nm, in some cases up to 100 nm, as determined by ellipsometry and atomic force microscopy (AFM; Figure 1 a). The PF2/6 films are strongly adherent and remain intact upon extensive rinsing with various organic solvents such as $CHCl_3$ and THF in an ultrasonic bath and Soxhlet apparatus. Since the consumption of the monomer upon the grafting is negligible, the reaction mixture can be used for many polymerizations. Importantly, an increase of the anchoring PS(Br) layer has only a small effect on the grafting process suggesting that the polycondensation proceeds predominantly from the topmost

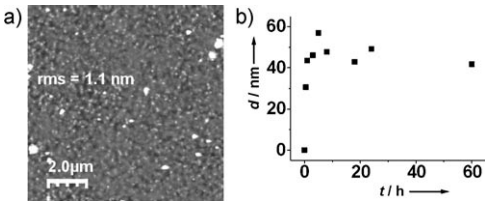

Figure 1. a) AFM topography image of 40 nm thick film of PF2/6 grafted from 2 nm thick PS(Br) film, b) kinetics of the grafting process. d = layer thickness, rms = route-mean square deviation as determined for the whole image.

part of the PS(Br) film, in contrast to our earlier Kumada SIP.[7] To analyze a kinetics of the grafting process, six silicon wafers and six glass slides coated each with 2 nm thick PS(Br) anchoring layers were prepared and the polymerization was conducted at different time from 0.5 to 60 h under otherwise identical conditions. We found that the resulting PF2/6 films reach the thickness of approximately 30 nm after 30 min of the polymerization, and approached maximal thicknesses within the first hour of polymerization (Figure 1 b, Supporting Information S8).[13]

The absorption and emission spectra of the grafted PF2/6 films in the dry state and in different solvents ($\lambda_{max} \approx 373$ nm; $\lambda_{em} \approx 413$ nm, 437 nm; Figure 2) are similar to the spectra of

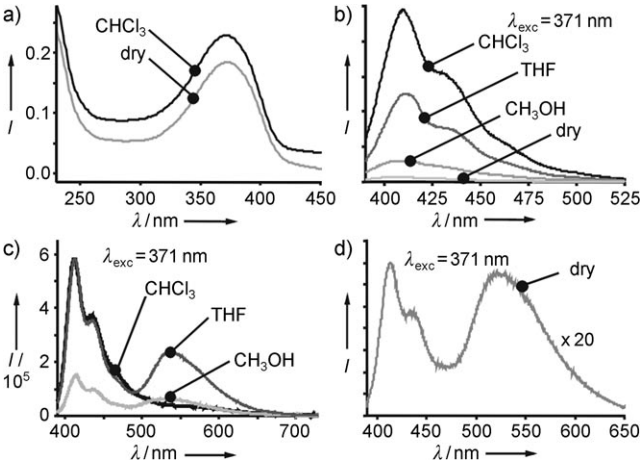

Figure 2. a) UV/Vis and b) fluorescence spectra of the 40 nm thick PF2/6 film grafted from 2 nm thick PS(Br). c,d) Fluorescence spectra of the same film aged during 2 h at 200 °C.

unbound, high MW PF2/6 (Supporting Information, Figure S10–12).[14] The absorption intensity for the grafted films approaches to the one for spin-coated PF2/6 films of the same thickness (Supporting Information, Figure S11) and all these data further confirm that the grafted material is PF2/6 (not in German version). As expected, the highest fluorescence intensity of the grafted PF2/6 was observed for the films immersed in $CHCl_3$, which is a good solvent for PF2/6. The emission intensity in THF was approximately 50 % of that in $CHCl_3$, and in methanol only 10 % of that in $CHCl_3$. The lowest fluorescence intensity (ca. 5 % of that in $CHCl_3$) was found for the grafted PF2/6 films in the dry state, likely, due to an aggregation of PF2/6 chains causing the well-known self-

quenching effect. The surface-grafted PF2/6 films do not exhibit degradation upon storage in contact with air for at least three month. However, air-annealing of the samples at 200 °C leads to appearance of a characteristic green emission, presumably, because of formation of fluorenone-defects ($\lambda_{max} = 522$ nm) in the PF2/6 structure (Figure 2c,d).[15] Compared to the emission around 413 nm, the green emission is stronger in the dry state, much lower in THF, and is completely suppressed in $CHCl_3$ suggesting that complete disaggregation of PF2/6 chains occurs only in the strongest solvent. The green emission recovers again after evaporation of $CHCl_3$ emphasizing that it is not solely the chain-aggregation effect, but a result of irreversible alterations of the chemical structure in the polymer backbone.

We further verified the applicability of our surface-initiated Suzuki chain-growth polycondensation for the preparation of PF2/6 patterns. Patterned structures of conjugated polymers are of significant interest for possible applications in sensors, catalysis, and optical devices. Surface and site-specific polymerization is an excellent tool for patterning of polymers. As a proof of principle for surface patterning we used a type of colloidal lithography in which sub-micrometer hydrogel particles were arranged on silicon wafers by dip coating and used as a mask (Supporting Information, Figure S13). Afterwards, the samples were treated by octadecylsilane (ODS) to deactivate (that is, to make hydrophobic) the space between the particles. After the removal of the particles, silane **2** was adsorbed selectively onto remaining hydrophilic spots. AFM reveals the successful microstructuring of **2** into a quasi-periodic hexagonal array of round-shaped disks approximately 1 μm in diameter (Figure 3a and Supporting Information, S14). Subsequent treatment of the samples with the palladium catalyst and the monomer solution results in selective grafting up to a thickness of 100 nm (Figure 3b,c).

In summary, we have developed the first surface-initiated and site-specific Suzuki polycondensation to fast and selectively graft polyfluorene from properly functionalized and (optionally) patterned surfaces at room temperature. We believe that the method will become a powerful surface-engineering tool, useful for fabrication of optoelectronic devices and sensors. In the next step, it would be desirable to develop grafting onto electrically conductive substrates for investigations into the electroluminescent properties of the grafted polyfluorenes, as well as to determine scope and limitation of the surface-initiated polycondensation.

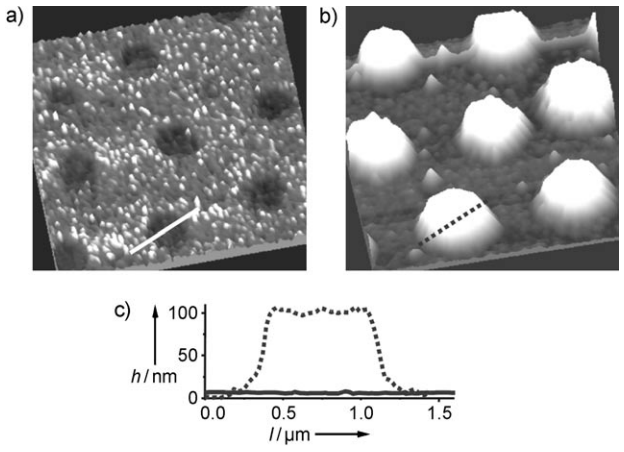

Figure 3. AFM topography images of a) silane **2**, b) grafted PF2/6, and c) cross-sections of patterned surfaces along the lines in (a) and (b); ——:2, •••••: PF2/6.

Experimental Section

Compounds **1** and **5** were prepared as described in refs. [9,10], respectively. Synthesis of **2** is given in Supporting Information. Other chemicals were supplied by Aldrich.

Grafting of PF2/6. Freshly cleaned with an NH_4OH/H_2O_2 mixture, highly polished Si wafers (Wacker-Chemitronics), glass or quartz slides (Menzel-Glaser) were used. A 1 nm thick PGMA layer was deposited by spin-coating from $CHCl_3$ (PGMA: poly(glycidyl methacrylate), 0.01 mg mL^{-1}, 2000 rpm) onto Si wafers, or glass slides and the samples were annealed at 150 °C for 10 h under an argon atmosphere. From 0.5 nm to 10 nm thick films of PS(Br) were then deposited by spin-coating (2000 rpm) from 0.01–0.2% solutions of PS(Br) in $CHCl_3$. Finally, the samples were irradiated with UV light for 30 s to cross-link the polymers, extensively rinsed with THF, and dried.

Deposition of silane **2**: Freshly cleaned samples were placed in a desiccator on the bottom of which a few drops of **2** was placed. The desiccator was closed and air was removed with the aid of a vacuum pump. The reaction was allowed to proceed for 2 h at room temperature. The samples were extensively rinsed with $CHCl_3$ and THF to remove physisorbed silane. The dried substrates coated with PS(Br) or **2** were placed into a round-bottomed flask equipped with a septum, and the atmosphere was replaced by argon. A solution of **3** in dry toluene (0.05 weight %, 10 mL) was added to the flack by syringe, the samples were allowed to react for 2 h at 70 °C. The samples were then washed twice in the glovebox with dry and deoxygenated toluene and twice in THF to remove the excess of residual **3**. Finally, the monomer **5** (0.02 g) in THF (10 mL) and a 2 M aqueous solution of Na_2CO_3 (3 mL) were added and the samples were gently stirred at room temperature. To stop polymerization, the samples were removed from the reactor and rinsed with 5 M HCl, water, and hot organic solvents ($CHCl_3$ and THF). Other experimental details, such as, materials, experimental techniques, XPS data, UV/Vis, fluorescence spectra of PF2/6, the patterning procedure and color versions of Figures 1 and 3 are given in the Supporting Information.

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