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Conductive Polymer Brushes of Regioregular Head-to-Tail Poly(3-alkylthiophenes) via Catalyst-Transfer Surface-Initiated Polycondensation

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Abstract: We describe a new method to grow conductive polymer (CP) brushes of regioregular head-to-tail poly(3-alkylthiophenes) (P3AT) via surface-initiated polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene. A simple procedure for the preparation of the Ni(II) macroinitiator by the reaction of $Ni(PPh_3)_4$ with photocross-linked poly-4-bromostyrene films was developed. Exposure of the initiator layers to the monomer solution leads to selective chain growth polycondensation of the monomer from the surface, resulting in P3AT brushes in a very economical way. In contrast to the P3AT films prepared by traditional solvent casting methods, our approach leads to mechanically robust CP films, stable against delamination. We believe that our approach will be helpful in the fabrication of all-plastic devices.

Introduction

This paper proposes new approach for growing thin conductive polymer films via surface-initiated polycondensation. In the first proof-of-concept example, we describe grafting of regioregular head-to-tail poly(3-hexylthiophene) (HT P3HT) from photocross-linked poly(−4-bromostyrene) (PS−Br) films. The process involves conjugated polymer catalyst-transfer chain growth polycondensation[1,2] of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1a**) selectively from the sites on the surface where the tetrakis(triphenylphosphine)-nickel(0), $Ni(PPh_3)_4$, catalyst was covalently immobilized.

Recently, surface-initiated polymerization leading to polymer brushes has become an area of great interest. Polymer brushes were grown on objects of different shapes and sizes and applied to the fabrication of stimuli-responsive surfaces,[3] drug delivery systems, control of adhesion,[4] lubrication, stabilization of nanoparticles, etc.[5] On the other hand, conductive polymers (CPs), and especially poly(3-alkylthiophenes) (P3AT), continue to attract the considerable interest of researchers due to their exceptional electronic and photonic properties largely depending on mesoscale organization of CPs.[6] We suggested that a combination of these two attractive issues might have a significant synergistic effect. For instance, the brush-like architecture of the CP films would have a beneficial effect on solar cell performance, if the CP chains can be grown directly from working electrodes, thus forming optimized bulk heterojunctions.[7] On the other hand, immobilization of CPs onto a solid support without a loss of their conformational freedom is a key step toward regenerable biological and chemical sensors.[8] In spite of its obvious promise, little research has been performed in the field of CP brushes[9] because of great difficulties in its preparation.[10,11]

The synthesis of vinyl polymers generally proceeds through an addition polymerization reaction and involves a chain growth polymerization mechanism, which itself is easily adaptable for initiating from surfaces or for the realization of controlled (living) polymerization schemes.[12] However, vinyl polymers represent a relatively small part of a broad population of polymers. Typically, the synthesis of a large number of

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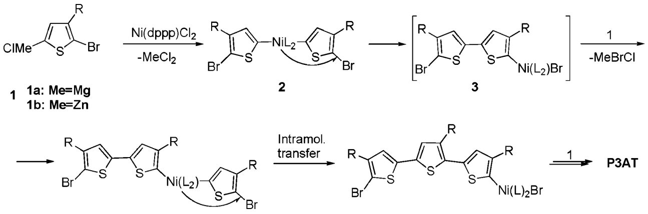
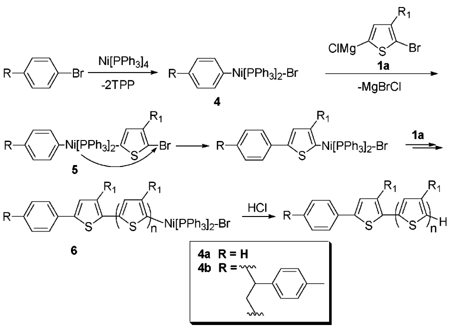
Scheme 1. Mechanism of Chain-Gowth Polycondensation of **1** According to McCullough et al.[1] and Yokozawa et al.[2]



Scheme 2. Polycondensation of **1a** Initiated by the Small Molecules or Macroinitiators



industrially important polymers (such as polyamides, polyesters, or electrically/optically active conjugated polymers) involves polycondensation reactions having a step growth polymerization mechanism.[13] In this case, polymer chains propagate randomly by the coupling of monomers and/or earlier formed oligomeric fragments via the abstraction of small molecules. Thus, even if an appropriate anchoring group (able to couple with the monomer) was immobilized on the surface, the process in the better case leads to the mixture of grafted chains and a large amount of unattached polymer. On practice, this approach fails to produce CP brushes with reasonable grafting densities since polymerization products form faster in solutions, precipitate onto the surface, and hinder growth from the surface. Thus, step growth polycondensations are hardly applicable for the synthesis of polymer brushes.[10]

A recent discovery made by McCullough et al.[1] and Yokozawa et al.[2] of the Ni-catalyzed chain growth polycondensation of **1a** to regioregular HT P3HT attracted our attention as a viable opportunity to develop surface-initiated polycondensation leading to CP brushes and other related polymer architectures. It was shown that the first step of the mechanism involves the preparation of the catalytic Ni(0) species from the catalyst precursor Ni(dppp)Cl$_2$ through the addition of two molecules of **1a** by their magnesium ends, yielding the symmetrical bisorganonickel compound **2** (Scheme 1).[1,2]

On the second stage, reduced Ni(0)dppp migrates to the nearest end of the molecule by the intramolecular insertion into the C−Br bond to form a tail-to-tail bithiophene **3** terminated by the Ni catalyst. Growth of the polymer chain occurs by the addition of one monomer at a time by its magnesium-terminated end to the Ni−Br bond of **3** followed by the intramolecular transfer of the Ni catalyst into the terminal C−Br bond. An alternative intermolecular transfer of the Ni catalyst into the C−Br bond of monomer **1a**, corresponding to the step growth polycondensation mechanism, is less favored here because of the deactivating character of the electron donating magnesium moiety in **1a**. Thus, the key peculiarity of the mechanism is that it involves the selective intramolecular insertion of the Ni catalyst to the more reactive end group of the polymer, resulting in one-by-one successive addition of monomers to the growing point of the polymer chain instead of the usual pathway for polycondensation random coupling.[14]

McCullough et. al demonstrated that this important feature of the mechanism gives access to various block copolymers, in which the first polymerized block is P3AT.[1,15] Our ultimate aim is to develop a complimentary process—a procedure allowing one to grow P3AT selectively from the initiator immobilized onto either planar surfaces, or spherical particles, or macromolecules, resulting in either flat CP brushes, or spherical CP brushes, or CP stars, or molecular brushes with CP side chains.

In general, for the realization of the surface-initiated polymerization, suitable initiators should be attached to the surface, and the polymerization reaction has to involve the chain growth mechanism. Since the synthetic procedure developed by McCullough et al.[1] and Yokozawa et al.[2] fulfills the crucial last requirement and can be realized in the near leaving manner, we first explored the possibility of employing the Ni(dppp)Cl$_2$ catalyst for the surface-initiated polymerization of **1a**. The key step here is the synthesis of the Ni-based initiator, having an aryl moiety attached to the surface and a halide group reactive toward Grignard reagents. The direct coupling of Ni(0) complexes with arylhalides, as shown in Scheme 2, would be one of the most straightforward and economical routes to the key organonickel initiator.[16] Unfortunately, Ni(dppp)$_2$, Ni(0) analogous to Ni(dppp)Cl$_2$, is not sufficiently reactive toward nonactivated arylhalides.[16] We therefore switched our attention to the more reactive Ni(PPh$_3$)$_4$ complex, which smoothly reacts with various arylhalides, giving the desired adducts (PPh$_3$)$_2$Ni(Ar)-Br (**4**).[17] In this work, we utilized easily available PS−Br for the preparation of the macroinitiator. To verify applicability of the Ni(PPh$_3$)$_4$-based initiators for surface-initiated polycondensation, we investigated the polymerization using bromobenzene (Ph−Br) and *o*-bromotoluene (*o*-Tol-Br) as small molecule models of PS−Br.

Replacing the classical Ni(dppp)Cl$_2$ catalyst by the less-studied Ni(PPh$_3$)$_4$, we were focused on the study of the polycondensation mechanism, having in mind that only the chain growth mechanism is desired for the synthesis of the polymer brushes. Another investigating issue was the regioregularity of the Ni(PPh$_3$)$_4$mediated polymerization products.

It was previously demonstrated that the degree of regioregularity of P3AT strongly depends on both metal and ligands of the catalytic complex. Rieke et al.[18] reported that the Ni(PPh$_3$)$_4$-catalyzed polycondensation of the mixture of **1b** (90%) and its regiomer 5-bromo-2-(bromozincio)-3-hexylthiophene **1b′** (10%), formed upon the treatment of 2,5-dibromo-3-alkylthiophene (**7**) with activated Zn, leads to P3HT with only 65% HT regioregularity. In contrast, Ni(dppp)Cl$_2$mediated polymerization of

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the same monomer mixture resulted predominantly in HT P3AT. The high HT regularity in the last case was provided by a selective consumption of only the major isomer **1b**. It was, however, not clear whether the reduced regularity of the Ni(PPh_3)$_4$ polymerized products was the result of an equal coupling of both isomeric monomers present in the reaction mixture or due to isomerization of the monomers during the coupling, in a manner similar to the Pd(PPh_3)$_4$-catalyzed polycondensation.[18] To distinguish between the mechanisms contributing to the decrease of the HT regularity, the polycondensation was investigated for pure isomer **1a** and a mixture of isomeric monomers.

Results and Discussion

Room-Temperature Polycondensation. Ni(PPh_3)$_4$ reacts with Ph−Br, giving (PPh_3)$_2$Ni(Ph)Br (**4**) within a few hours at room temperature. The polymerization of **1a**, prepared from equimolar amounts of 2-bromo-3-hexyl-5-iodothiophene (**8**) and *t*-BuMgCl, was performed at room temperature for 4 h in the presence of 1.67 mol % of **4**. The reaction mixture was quenched with 5 M hydrochloric acid, as proposed by Yokozawa et al.[2] and washed with methanol. P3HT was isolated with ≈70% yield (conversion of **1a** ≈80%).

Detailed assignment and integration of all signals in the aromatic region of the ^{1}H NMR spectrum give quantitative information about both starting groups and end groups of the resulting P3HT products (Figure 1a). Assuming that all P3HT chains are terminated by either hydrogen or bromine atoms, it was calculated that at least 55% of P3HT molecules has a Ph starting group. Thus, a significant P3HT fraction (≈45%) does not contain the Ph group. According to MALDI-TOF, the content of the Ph-initiated P3HT is higher. As shown in Figure 1b, ≈80% of P3HT is terminated by the Ph group from the one side and by either hydrogen or bromine atoms at the opposite terminus (67% of Ph/H and 13% of Ph/Br P3HT). The minor fraction of P3HT (≈20%), which falsified the NMR calculation, contains hydrogen atoms on both ends (H/H P3HT).[19] The molecular weight of the resulting P3HT determined by GPC ($M_n = 4100$ g/mol, $M_w = 8100$ g/mol) is lower than could be predicted for living polymerizations for the given feed ratio and the monomer conversion (feed ratio **1a**/**4** = 60:1, conversion of **1a** ≈80%; $M_{n,\text{living}} = 8000$ g/mol; $DP_{\text{step}} = 60 \times 0.8 = 48$). On the other hand, the measured value of M_n is much higher than expected for the step growth polycondensations at ≈80% conversion of **1a** ($M_{n,\text{step}} = 830$ g/mol; $DP_{\text{step}} = 1/1-0.8 = 5$).

All these data allow us to conclude that the polycondensation begins from the initiator **4** and involves a chain growth mechanism, giving predominantly Ph/H-terminated P3HT upon hydrolysis of the C−Ni bond of the intermediate **6**. This reaction, however, is not so perfect as the near living Ni(dppp)-Cl_2− catalyzed polymerization, and a significant fraction of the growing chains terminates before the complete conversion of the monomer, resulting in Ph/Br-terminated P3HT. The presence of the bromine group in the polymer end is an indicator of the chain-transfer termination step, when the Ni catalyst undergoes intermolecular transfer instead of intramolecular transfer, the C−Br end bond remaining intact. Obviously, H/H-terminated P3HT is the result of newly initiated polymerization, catalyzed by the escaped Ni catalyst.[20] MALDI-TOF spectra confirm this assumption, showing that the content of H/H-terminated P3HT is maximal in the low molecular weight P3HT fraction (≈60% of H/H P3HT for M_n ≈1100 g/mol vs ≈15% for M_n ≈6000 g/mol). A relatively high polydispersity (PDI ≈1.9) and the lower than expected molecular weight of the resulting P3HT corroborate with the imperfect chain growth polymerization.

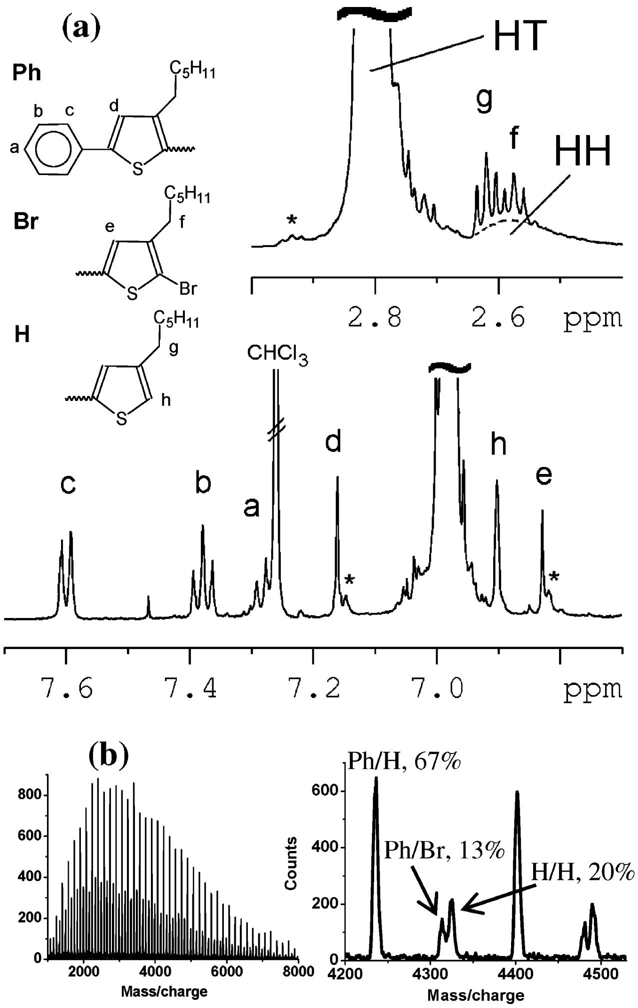

Figure 1. (a) Regions of the ^{1}H NMR spectrum showing the signals of the starting group Ph and the end groups Br and H (a−h) and the α-methylene groups of regioregular (HT) and head-to-head (HH) sequences (*: ^{13}C satellites) and (b) MALDI-TOF spectra of P3HT obtained upon the polymerization of **1a** and 1.67 mol % of **4** at room temperature for 4 h.

Low Temperature Polycondensation. Lowering of the temperature from RT to 0 °C has a positive effect on the control of the polymerization process. According to MALDI-TOF spectra, the reaction mixture obtained upon the polymerization of **1a** in the presence of 3.56 mol % of **4** (feed ratio of 28:1, conversion of **1a** ≈95%) at 0 °C for 6 h contains only traces of P3HT terminated by hydrogen atoms from both sides (2% of H/H P3HT). The main product here is Ph-terminated P3HT (78% of Ph/H P3HT and 20% of Ph/Br P3HT, Figure 2). As it follows from the MALDI-TOF, GPC, and NMR data, the

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(19) To further prove that the peaks with $m/z = (166.28n + 1 + 77)$ in the MALDI-TOF spectra indeed correspond to Ph/H P3HT, and not to Br/H P3HT with similar m/z values, we also used (PPh_3)$_2$Ni(*o*-Tol)Br as the initiator instead of (PPh_3)$_2$Ni(Ph)Br. As expected, the main sets of peaks corresponding to Ar/H and Ar/Br P3HT were shifted by 15 Da.

(20) The exact mechanism of the termination reactions remains unclear.

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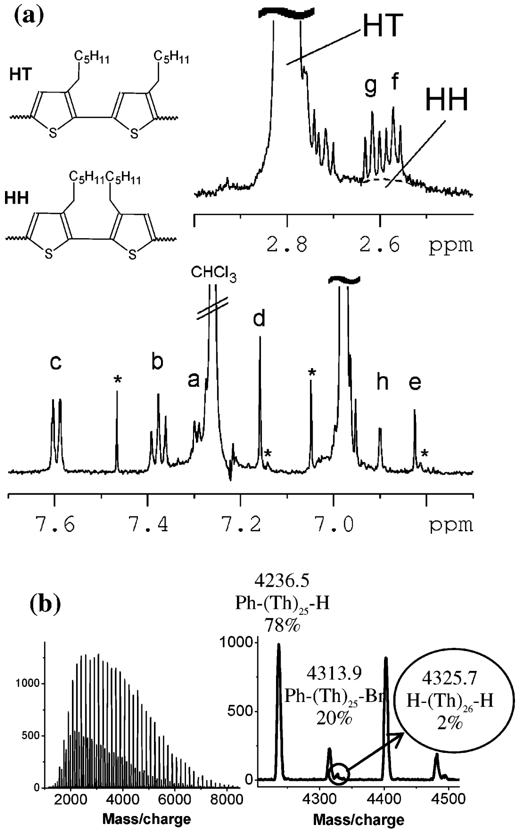

Ph-(Th)$_{25}$-H 4236.5: (166.3•25+77+1=4235.5)

Ph-(Th)$_{25}$-Br 4313.9: (166.3•25+77+79.9=4314.4)

H-(Th)$_{26}$-H 4325.7: (166.3•26+2=4325.8)

Figure 2. (a) Regions of the ^{1}H NMR spectrum showing the signals of the starting group Ph and the end groups Br and H (a−h, compare also Figure 1a) and the α-methylene groups of the major regioregular (HT) and the very low head-to-head (HH) sequences (*: ^{13}C satellites) and (b) MALDI-TOF spectra of P3HT obtained upon the polymerization of **1a** and 3.56 mol % of **4** at 0 °C for 6 h.

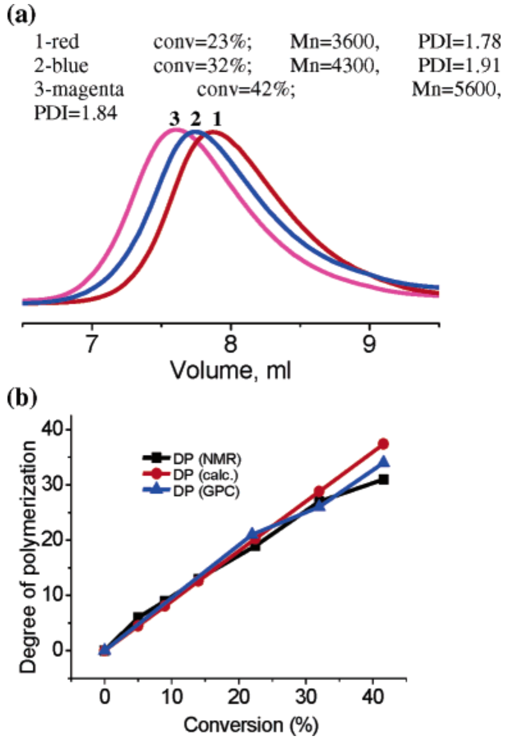

Figure 3. (a) Gel permeation chromatography traces for polymerization of **1a** in the presence of 1.11 mol % of $(PPh_3)_2Ni(o\text{-}Tol)Br$ at 0 °C. (b) Dependence of DP on conversion for the same experiment: red line—theoretical dependence for an ideal living polymerization for the giving feed ratio; blue line—the dependence from GPC data; and black line—the dependence from ^{1}H NMR data.

molecular weight of the obtained polymer ($M_{n,MALDI} = 3845$ g/mol; $PDI_{MALDI} = 1.12$; $M_{n,GPC} = 5500$ g/mol; $PDI_{GPC} = 1.44$; $DP_{NMR} = 29$; $M_{n,NMR} = 4900$ g/mol) approaches the theoretical value, which can be predicted assuming the living polymerization mechanism for the given feed ratio ($M_{n,calc} = 4656$ g/mol). A preliminary kinetic study performed for the polymerization of **1a** initiated by 1.11 mol % of bis(triphenylphosphine)*ortho*-tolylbromonickel(II), $(PPh_3)_2Ni(o\text{-}Tol)Br$, (feed ratio of 90:1) at 0 °C confirms the chain growth mechanism (Figure 3 and Supporting Information). Determination of the monomer conversion for different stages of the polymerization was performed by the detailed analysis of the sampled fractions by ^{1}H NMR. The molecular weight of the P3HT fractions was evaluated by ^{1}H NMR and GPC. A slight deviation of the molecular weight versus monomer conversion plot from the typical plot for living polymerization linear dependence indicates the existence of termination reactions (Figure 3b).

Regularity. To our surprise, a relatively high HT regularity of 91−95% was found for the resulting P3HT obtained at room-temperature polycondensations of pure isomer **1a** initiated by **4** (Figure 1a). Furthermore, a decrease of the polymerization temperature to 0 °C results in an increase of the HT regularity up to nearly 100% (Figure 2a). This result demonstrates that $Ni(PPh_3)_4$- and $Ni(dppp)Cl_2$-based catalysts behave similarly at low temperatures, inducing polycondensation of the monomers without their isomerization. The difference, however, is in the reactivity of $Ni(PPh_3)_4$- and $Ni(dppp)Cl_2$-based intermediates. As it was earlier demonstrated, the $Ni(dppp)Cl_2$ complexes differentiate isomeric monomers **1a** and **1a′** involving selectively the isomer **1a** into the polymerization. In contrast, the $Ni(PPh_3)_4$-based initiator is less selective and gives fully regular HT-P3HT only from pure **1a**. $(PPh_3)_2Ni(Ph)Br$− mediated room-temperature polycondensation of the mixture of isomers **1a** (75%) and **1a′** (25%), obtained from dibromide **7**, leads to P3HT with an HT regularity of ≈70%. A decrease of the polymerization temperature to 0 °C, however, enhances HT regularity up to 85% due to a preferential consumption of the **1a** monomer.

Intermediate Conclusions. Thus, we can conclude that the $Ni(PPh_3)_4$-based initiators constitute a good compromise between reactivity and selectivity in the polycondensation reactions of thiophenes. Because of the high reactivity of $Ni(PPh_3)_4$, various Ni initiators can be prepared from easily available arylhalides. At the same time, the reduced selectivity of the $Ni(PPh_3)_4$-based intermediates resulting from enhanced mobility of its ligands can be efficiently compensated, and undesired termination reactions can be suppressed by the lowering of the polymerization temperature and employing pure monomers. In that case, the polycondensation involves the chain growth mechanism and leads to fully regioregular P3AT. This is a good starting point to employ the process for the preparation of P3AT brushes.

P3HT Brushes. In the next step, we explored the possibility of preparing P3HT brushes via surface-initiated polycondensation of **1a** from surface-immobilized macroinitiators. To enhance

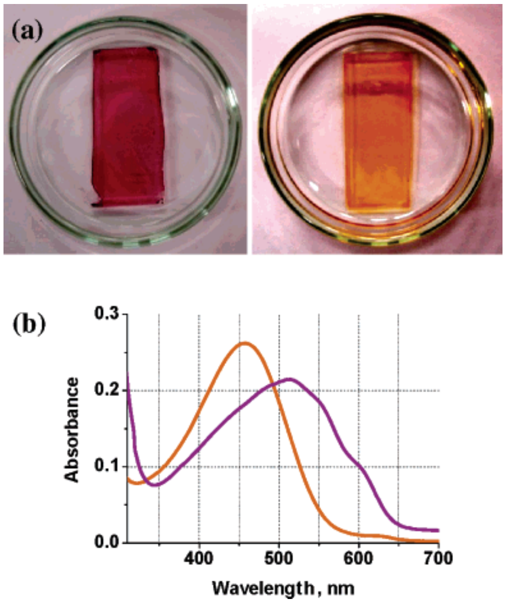

Figure 4. (a) Photographs of the 60 nm thick HT P3HT brush grafted to a glass slide in dry state (left) and in chloroform (right). (b) UV−vis absorption spectra of the HT P3HT brush in the dry state (violet) and in chloroform (orange).

an adhesion of PS−Br to the substrate, 2 nm thick poly(glycidyl methacrylate) (PGMA) films were spin-coated onto freshly cleaned Si wafers or glass slides and then annealed. PS−Br was deposited afterward by spin-coating from a solution in CHCl$_3$. Finally, PS−Br layers were cross-linked by irradiation with UV light, extensively rinsed with THF, and dried. We found that the thickness of at least 30 nm of the PGMA/PS−Br anchoring layer was required to achieve its stability under the polymerization conditions. The samples were placed into the round-bottomed flask under argon atmosphere, the Ni(PPh$_3$)$_4$ solution was added, and the samples were allowed to react overnight at room temperature. The samples were then extensively washed with THF to remove the excess of unreacted Ni(PPh$_3$)$_4$. Afterward, the solution of the monomer **1a** in dry THF was added, and the samples were allowed to polymerize at 0 °C.

It is important to note that the polymerization proceeds selectively from the immobilized initiator and not in the bulk solution. The procedure results in smooth, uniform, and strongly adherent P3HT films, which pass a peel test with Scotch tape and remain intact upon extensive rinsing with various organic solvents in an ultrasonic bath and Soxhlet apparatus. The thicknesses of the resultant P3HT brushes grown from 30 to 40 nm thick PGMA/PS−Br anchoring layers were typically between 40 to 70 nm depending on the polymerization conditions. The violet color of the P3HT films grown on the glass slide in a dry state was similar to the color of commercial HT P3HT deposited by spin-coating. This is an indication of the regioregularity and high molecular weight of the grafted HT P3HT. The brushes grafted to glass slides display solvatochromism and thermochromism similarly to the dissolved P3AT. P3HT brushes change from orange when being placed in chloroform, which is a good solvent for P3HT ($\lambda_{max} = 442$ nm), to violet ($\lambda_{max} = 515$ nm) in the dry state or in methanol (bad solvent) (Figure 4). The observed red shift and appearance of shoulders at $\lambda = 550$ and 610 nm in the UV−vis spectra are due to a transition from less conjugated (twisted) to more

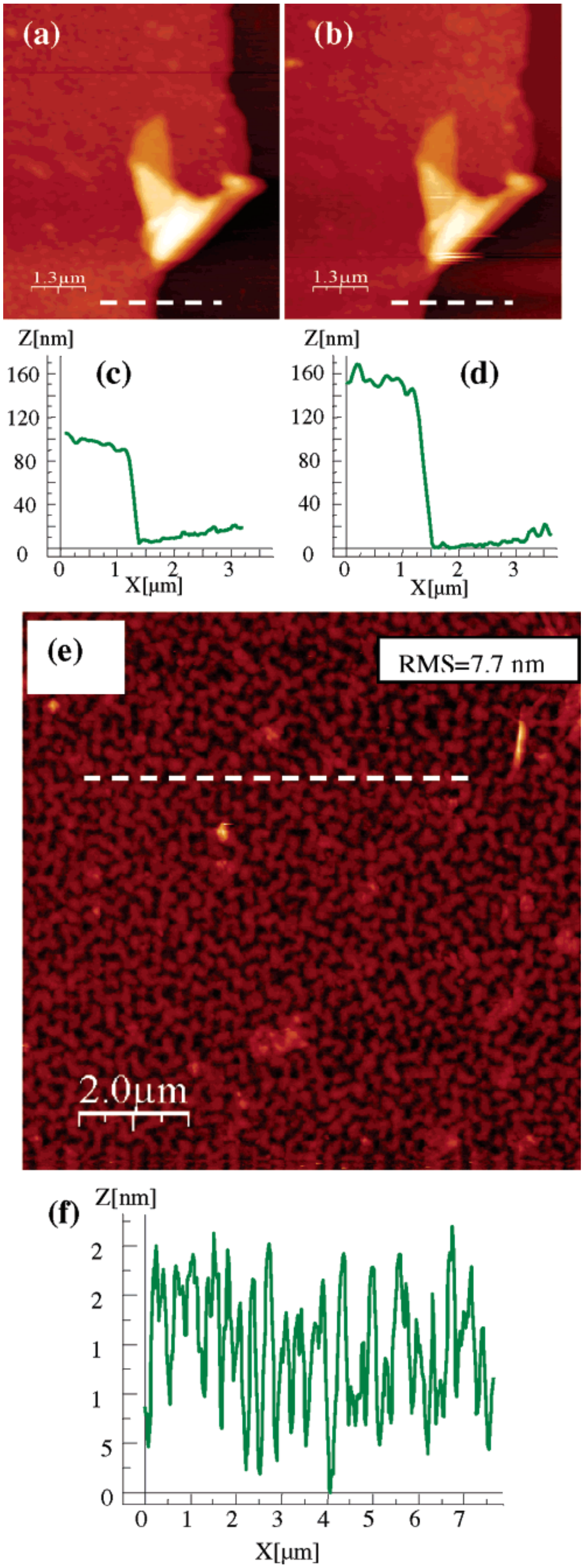

Figure 5. AFM images (a and b) and cross-sections (c and d) of the scratched area of the 60 nm thick P3HT brush grown from the 40 nm thick PGMA/PS−Br anchoring layer: (a and c) in dry state and (b and d) in xylene vapors. 10 μm × 10 μm AFM topography image (e) and cross-section (f) of the P3HT brush.

conjugated (planar) conformations, which is an usual phenomenon for the regioregular HT P3ATs. These results imply a conformational freedom of P3HT chains despite the fact that they are tethered to the substrate.

A swelling behavior of the P3HT brushes was studied with the aid of atomic force microscopy (AFM). Figure 5 shows AFM images of the scratched area of the 65 nm P3HT brush grown from a 35 nm thick film of PGMA/PS−Br in both dry state and xylene vapors (good solvent for P3HT and PS−Br). As seen from the cross-sections (Figure 5c,d), the film thickness increases from about 100 nm in the dry state to 160 nm in the saturated xylene atmosphere. Similar swelling experiments were also performed for the starting 35 nm thick PGMA/PS−Br anchoring layer. This film swells in xylene by 20 nm (from 35 to 55 nm, AFM data not shown). Assuming swellability of the anchoring PGMA/PS−Br layer inside the composite PGMA/PS−Br/P3HT film to be approximately the same as for PGMA/PS−Br alone, the contribution of the P3HT component into the overall swelling of the PGMA/PS−Br/P3HT film is only about 40 nm (20−−60 nm). This relatively low swellability of the P3HT brush (from 65 to 105 nm) can be explained by relatively high rigidity of the polythiophene backbone and/or high grafting density of the brush. From the thickness of the swollen brush (105 nm) and knowing the length of the thiophene monomer unit (0.38 nm), the DP of the grafted P3HT chains can be estimated to be at least 276. Careful inspection of the P3HT brushes by tapping mode AFM revealed their lamellar morphology (Figure 5e), although the starting PGMA/PS−Br anchoring layers display featureless morphology. Similar lamellae structures were previously observed for the films of regioregular HT P3HT prepared by the solvent casting method.[6b,23] Previously, a microphase separation was observed in bicomponent polymer brushes due to the incompatibility of the polymers composing the brush, whereas monocomponent brushes usually display featuresless morphology.[3] The observed structuring of the monocomponent P3HT brushes found here might be explained by the amphiphilic nature of P3HT and by a strong tendency of polythiophenes to form rod-like semicrystalline aggregates due to π-stacking interactions.[6b,23]

Electrical conductivity was measured for P3HT brushes prepared on glass slides. In-plane conductivity of the 65 nm thick P3HT brush atop the 35 nm thick anchoring layer significantly increased after doping with $FeCl_3$ solution and reached a value of about 2 S/cm^{-1}. Extensive characterization of the P3HT brushes will be published elsewhere.

Conclusion

This paper describes a new method to grow conductive polymer brushes of regioregular head-to-tail poly(3-alkylthiophenes) via surface-initiated polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene. We developed a simple procedure for the preparation of the Ni(II) macroinitiator by the reaction of $Ni(PPh_3)_4$ with photocross-linked poly(−4-bromostyrene) films. Exposure of the initiator layer to the monomer solution leads to selective polymerization of the monomer predominantly from the surface and not in the bulk solution, resulting in conductive polymer brushes in a very economical way. In contrast to the P3AT films prepared by traditional solvent casting methods, our approach gives access to mechanically robust conductive polymer films, stable against delamination. Having in mind a high processability of PS−Br and its copolymers along with the possibility of applying various standard lithography methods (such as contact molding or photolithography) to PS−Br, we believe that our approach represents a new dimension in the fabrication of all-plastic devices.

Investigation of the polymerization mechanism reveals that the $Ni(PPh_3)_4$ mediated polycondensation involves, rare for the chemistry of conductive polymers, a chain growth mechanism, which was observed earlier only for the polymerizations mediated by the less reactive $Ni(dppp)Cl_2$ catalyst. We believe that this fact together with the ability of $Ni(PPh_3)_4$ to react easily with various arylhalides forming the initiators might allow us to use earlier inaccessible polymer architectures comprising conjugated polymers. According to existing strategies to such block copolymers, a properly terminated conjugated polymer must be prepared in the first step, and then other polymer blocks (usually nonconductive) can be polymerized from (or attached to) the reactive sites of the first CP block.[15,21] These strategies, however, are hardly applicable for selective synthesis of comb-like or star copolymers with CP side chains.[22] We believe that our method would be a basis of the alternative synthetic strategy, according to which P3AT might be selectively grown from any objects terminated by arylhalide groups reactive toward $Ni(PPh_3)_4$.

Experimental Procedures

Materials. *tert*-Butylmagnesium chloride (2.0 M solution in THF), tetrakis(triphenylphosphin)-nickel(0), bromobenzene, naphthalene, 4-bromostyrene, and dry tetrahydrofuran (stabilizer-free, anhydrous) were purchased from Aldrich and used as received without further purification. Poly(glycidyl methacrylate) ($M_n = 65\,000$ g/mol, PDI = 2.05) was purchased from Polymer Source Inc. Poly(−4-bromostyrene) ($M_n = 51\,000$ g/mol, PDI = 2.05) was obtained via radical polymerization of 4-bromostyrene.[24] 2-Bromo-3-hexyl-5-iodothiophene and 2-bromo-5-chloromagnesio-3-hexylthiophene were prepared as previously described.[2]

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.13 MHz for ^{1}H and at 125.23 MHz for ^{13}C using $CDCl_3$ as the solvent. The spectra were referenced on the solvent peak ($\delta(^1H) = 7.26$ ppm; $\delta(^{13}C) = 77.00$ ppm). 2-D spectra (COSY, TOCSY, tr-NOESY, HMQC, and HMBC) were recorded using the standard pulse sequences of the Bruker software.

UV−vis measurements were carried out using a PerkinElmer UV−vis Spectrometer Lambda 800.

GPC measurements were carried out on Knauer, a Hewlett-Packard normal-temperature size exclusion chromatograph, equipped with refractive index detector and two columns of PL MIXED-C (Polymer Laboratories Ltd.); eluent was chloroform. Calibration was based on polystyrene standards obtained from Polymer Standards Service.

MALDI-TOF mass spectra were recorded on a Bruker Daltonics biflex IV mass spectrometer. Experiments were performed with an accelerating potential of 20 kV in the reflectron mode collecting positive ions. Samples for measurements were prepared in $CHCl_3$ by mixing 5 μL of polymer solution with 50 μL of matrix (dithranol) solution. A total of 1 μL of this mixture was deposited on the plate, and after evaporation of the solvent, measurements were performed under high

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vacuum. To produce the final spectrum, mass spectra from 120 shots were accumulated. PEG was used as an external standard.

Ellipsometry. The thickness of the polymer films was measured by an SE400 ellipsometer (SENTECH Instruments GmbH) with a 632.8 nm laser at a 70° incident angle.

AFM Measurements. Multimode AFM instrument (Digital Instruments) was operated in the tapping mode. Silicon tips with a 10−20 nm radius, a spring constant of 30 N/m, and a resonance frequency of 250−300 kHz were used.

Preparation of the Low Molecular Weight Initiator (4).[16] To a solution of $Ni(PPh_3)_4$ (222 mg, 0.2 mmol) in dry toluene (3.5 mL, glovebox, argon atmosphere), bromobenzene (0.1 mL, 0.95 mmol) was added at room temperature. The homogeneous mixture was stirred for 15 min and was allowed to stand unperturbed overnight. The original deep red color of the reaction mixture gradually changed to brownish-yellow together with the precipitation of **4** in the form of brownish-yellow crystals, which were separated by filtration, washed with dry hexane, and dried in a vacuum. Yield: 0.07 g, 47%.

Low Temperature Polymerization. 2-Bromo-3-hexyl-5-iodothiophene (**7**) (373 mg, 1 mmol) was placed in a round-bottomed flask equipped with a magnet stirrer bar, and the atmosphere was replaced with argon. Dry THF (20 mL) was added via a syringe, and the mixture was cooled to 0 °C. Afterward, isopropylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) was added via a syringe, and the mixture was stirred at 0 °C for 1 h. A solution of **4** in toluene (26.4 mg in 1 mL, 3.56 mol %) was added via a syringe at 0 °C, and then the mixture was stirred for 6 h at 0 °C. The reaction mixture was quenched by 5 M hydrochloric acid, and the products were extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Finally, MeOH was added to the residue, and the insoluble material was washed with MeOH and collected by filtration under vacuum to give pure P3HT as a purple solid (122 mg, 74%).

Preparation of P3HT Brushes. Highly polished Si wafers (Wacker-Chemitronics) or glass slides (Menzel-Glaser) were first cleaned in an ultrasonic bath 3 times for 5 min with dichloromethane, placed in a cleaning solution (prepared from NH_4OH and H_2O_2) for 1 h, and finally rinsed several times with Millipore water (18 MΩ × cm). The 2 nm thick film of poly(glycidyl methacrylate) PGMA (ellipsometry data) was deposited by spin-coating from chloroform (0.03 mg/mL, 2000 rpm), and the samples were annealed at 150 °C for 10 h in argon atmosphere. The 30 nm thick film of PS−Br was deposited afterward by spin-coating (2000 rotations/min) from 0.1 to 1% 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.

The samples were placed into the round-bottomed flask equipped with a septum, and the atmosphere was replaced with argon. Afterward, a solution of $Ni(PPh_3)_4$ in dry toluene (0.05 wt %, 10 mL) was added to the flask via a syringe, and the samples were allowed to react overnight at room temperature. The samples were then washed twice with dry THF to remove the excess of unreacted $Ni(PPh_3)_4$. For this, the reaction mixture was removed by the syringe, and a new portion of THF was added to the flask to fully cover the samples, stirred for few minutes, and then removed. The solution of **1a** in dry THF was added to the samples with immobilized initiator and stirred for several hours. Finally, the samples were extensively rinsed with 5 M HCl, water, methanol, and $CHCl_3$ and dried.

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Supporting Information Available: ^{1}H and ^{13}C NMR characterization, description of the kinetic experiment, and GPC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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