Macromolecules **2008**, *41*, 7383−7389

Grafting of Poly(3-hexylthiophene) from Poly(4-bromostyrene) Films by Kumada Catalyst-Transfer Polycondensation: Revealing of the Composite Films Structure

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Received April 22, 2008; Revised Manuscript Received July 16, 2008

ABSTRACT: In order to achieve a stable, long-term operation of flexible electronic devices, it is necessary to firmly fix semiconductive conjugated polymers to plastic substrates, thus preventing their damage against delamination or chemical treatments. Surface-initiated Kumada catalyst-transfer polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene from photo-cross-linked poly(4-bromostyrene), PS(Br), films leads to covalent grafting of regioregular head-to-tail poly(3-hexylthiophene), P3HT. Herein, we investigate the grafting process in detail and elucidate the structure of the resulting composite films using ellipsometry, X-ray photoelectron spectroscopy, Rutherford backscattering spectroscopy, and conductive mode atomic force microscopy techniques. In particular, we found that the grafting process is much more efficient if thick PS(Br) supporting layers are used. The maximal reachable thickness of the P3HT deposits is directly proportional to the thickness of the supporting PS(Br) layers. The obtained data suggest that the grafting process occurs not only at the PS(Br)/polymerization solution interface but also deeply inside the swollen PS(Br) films, penetrable for the catalyst and for the monomer. The process results into a kind of interpenetrated PS(Br)/P3HT network in which relatively short (∼10 nm) P3HT grafts emanate from long cross-linked PS(Br) chains. The films show good stability against delamination, high electrical conductivity in the doped state, and high swellability that might be exploited for construction of fully “plastic” electronic devices and sensors.

Introduction

Conjugated (or conductive) polymers[1] attract enormous attention of researchers as potentially low-cost materials for energy conversion, for construction of electronic devices, sensors,[2] and novel stimuli-responsive materials.[3] One of the key goals for research in this field is high-performance, fully plastic electronic devices.[4] To achieve a stable, long-term operation of flexible devices, conjugated conductive polymers must be firmly fixed to plastic substrates, thus preventing their damage against delamination or chemical treatments (e.g., upon patterning). Various methods for grafting of intrinsically insoluble conductive polymers, (e.g., poly(3,4-ethylenedioxythiophene),[5] polypyrrole,[6] polyaniline,[7] etc.) were already developed. Such polymers in a doped state act as highly efficient permanent conductors,[8] whereas their performance in undoped, semiconducting state is less attractive.[9] Owing their excellent semiconducting properties and air stability, regioregular polyalkythiophenes and their copolymers[10] are among the best organic materials for fabrication of field-effect transistors[11] and solar cells.[12] Although an approach to graft soluble *regioirregular* polyalkythiophenes by oxidative polymerization was developed,[13] covalent immobilization of their *regioregular* counterparts is a challenge.

In contrast to chain growth polyaddition reactions[14] that provide an easy access to various nonconductive polymer brushes,[15] synthesis of most conductive polymers follows a step growth polycondensation scheme.[16] This kind of polymerization is hardly applicable for the preparation of polymer brushes by a “grafting-from” approach, whereas a “grafting-to” method is also problematic in the case of conjugated polymers.[17] Recently, McCullough et al.[18] and Yokozawa et al.[19] made an important discovery that Ni-catalyzed Kumada[20] catalyst-transfer polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene (**1**) into regioregular poly(3-hexylthiophene) (P3HT) involves not the step growth mechanism, as it was believed for decades, but instead proceeds in a chain growth manner. Very recently, we made a step further and developed surface-initiated polycondensation, allowing one to grow P3HT from photo-cross-linked poly(4-bromostyrene), PS(Br), films.[21] The process involves Kumada catalyst-transfer polycondensation of **1** regioselectively from sites on the surface where $Ni(PPh_3)_4$ catalyst is covalently immobilized and no polymer is formed in the bulk solution. According to this method, P3HT layers with the thickness exceeding 50 nm and with the conductivity in doped state up to 2 S/cm were grown from relatively thick cross-linked PS(Br) films, whereas the grafting from rather thin PS(Br) layers was much less efficient.[21] We tentatively attributed this effect to insufficient mechanical stability of the films under the polymerization conditions, if thin anchoring layers are used. In the present paper we report on detail investigations of the grafting process and elucidate the structure of the resulting composite films using ellipsometry, X-ray photoelectron spectroscopy, Rutherford backscattering spectroscopy, and conductive mode atomic force microscopy techniques.

Experimental Part

Materials. *tert*-Butylmagnesium chloride (2.0 M solution in tetrahydrofuran, THF), tetrakis(triphenylphosphine)nickel(0) ($Ni(PPh_3)_4$), 4-bromostyrene, toluene, chloroform, and dry THF (stabilizer-free, anhydrous) were purchased from Aldrich and used as received without further purification. Poly(glycidyl methacrylate) (number-average molecular weight, $M_n = 65\,000$ g/mol, polydispersity index, PDI = 2.05) was purchased from Polymer Source Inc. Poly(4-bromostyrene) (PS(Br), $M_n = 51\,000$ g/mol, PDI = 2.05) was

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10.1021/ma800889c CCC: $40.75

obtained via radical polymerization of 4-bromostyrene (see Supporting Information).[22] 2-Bromo-3-hexyl-5-iodothiophene and 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) were prepared as previously described.[19]

Grafting of P3HT. Highly polished Si wafers (Wacker-Chemitronics) or glass slides (Menzel-Glaser) were first cleaned in an ultrasonic bath three times for 5 min with dichloromethane, placed in cleaning solution (prepared from NH_4OH and H_2O_2) for 1 h, and finally rinsed several times with Millipore water (18 MΩ cm). Poly(glycidyl methacrylate) layers of the same 2 nm thickness (ellipsometry data) were used in all experiments as adhesion promoter between PS(Br) and Si substrates. They were deposited by spin-coating from chloroform (0.03 mg/mL, 2000 rpm), and the samples were annealed at 150 °C for 10 h in an argon atmosphere. PS(Br) layers with the variable thickness from 1 to 200 nm were spin-coated onto poly(glycidyl methacrylate) from chloroform and cross-linked upon a brief irradiation (from 5 to 200 s, depending on the PS(Br) thickness) with UV light to achieve their insolubility, while remaining the films still swellable in "good" for PS(Br) solvents. The samples were extensively rinsed with THF, dried, and 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 repeatedly washed in the glovebox with dry and deoxygenated THF to remove the excess of unreacted $Ni(PPh_3)_4$. To this end, the reaction mixture was removed by the syringe, and the new portion of THF was added to the flask to fully cover the samples, stirred for few minutes, and then removed. Finally, the 15 mmol/L solution of the monomer **1** in dry THF was added, and the samples were polymerized at 0 °C for 10 h to achieve a maximal thickness of grafted P3HT.

Dry State Ellipsometry Thickness Measurements. The thickness of polymer layers in the dry state was measured by an SE400 ellipsometer (SENTECH Instruments GmbH, Germany) with a 632.8 nm laser at a 70° incident angle. A multilayer model has been used for calculation of the thickness of multicomponent polymer films from the ellipsometric angles Ψ and Δ. Initially, the thickness of the native SiO_2 layer was calculated at refractive indices $n = 3.858 - i \times 0.018$ and $n = 1.4598$ for the Si wafer and the SiO_2 layer, respectively. The thickness of the poly(glycidyl methacrylate) layer was evaluated using the two-layer model Si/SiO_2/poly(glycidyl methacrylate) with $n = 1.525$ for poly(glycidyl methacrylate).[23a] The thickness of the PS(Br) layer was evaluated using the three-layer model Si/SiO_2/poly(glycidyl methacrylate)/PS(Br) with $n = 1.63$ for PS(Br) (as measured for a 100 nm thick film). Since no option for the incorporation of the fourth layer in the program package, the thickness of the grafted P3HT layer was evaluated using the three-layer model, Si/SiO_2/[poly(glycidyl methacrylate) + PS(Br)]/P3HT with $n = 1.99$ for P3HT.[23b] In this model we considered poly(glycidyl methacrylate) + PS(Br) as a single layer with the n value, averaged according to the relative contribution of the poly(glycidyl methacrylate) and the PS(Br) components. In most cases PS(Br) was a major component and therefore n was close to 1.63. The measurements were averaged for at least 10 points for each sample.

Swellability Experiments. In order to examine the swelling behavior of the polymer layers in THF and toluene, the measurements were carried out using a null ellipsometer in a polarizer−compensator−sample analyzer (Multiscope, Optrel Berlin) mode. As light source a He−Ne laser with $\lambda = 632.8$ nm was applied, and the angle of incidence was set to 70°. An ellipsometric cell with thin glass walls, fixed at a known angle (68°) from the sample plane, was used.[23c] The angle of incidence of the light was set such that its path was normal to the window. The bilayer model (silicon/silicon oxide/swollen polymer film) was used to calculate the thickness of the swollen layer from the ellipsometric angles.[24] Since in the swollen state the films displayed rather large thickness (few hundreds of nanometers), it was possible to determine simultaneously the refractive index for the swollen film and their thickness.

Doping Procedure. PS(Br)/P3HT composite films prepared on glass slides as described above were dipped into a solution of $FeCl_3$ (10 g/L) in a methanol−THF mixture (2/1 v/v) for 15 min, extensively rinsed with methanol and THF, and dried. It was found that prolonged doping does not result in higher conductivities.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy spectra were recorded on AXIS ULTRA (Kratos Analytical, England) spectrometer using a mono-Al $K\alpha_{1,2}$ X-ray source operating at 300 W and 20 mA (see also Supporting Information). Five samples that allowed monitoring of all chemical transformations were prepared on poly(glycidyl methacrylate)-modified Si wafers: (1) 40 nm thick PS(Br); (2) the same as (1), but activated with $Ni(PPh_3)_4$; (3) the same as (2), but after the grafting of 90 nm of P3HT; (4) the sample analogous to (3), followed by Ar plasma etching of 20 nm in "mild" conditions (vide infra); (5) the sample analogous to (3), but 30 nm was etched in "hard" conditions.

Argon plasma etching was carried out in a computer-controlled MicroSys apparatus by Roth & Rau (Wüstenbrand, Germany) that is described in detail elsewhere.[25] "Mild" etching conditions: a 2.46 GHz microwave plasma (pressure 5×10^{-3} mbar, effective power 100 W, sample placed on a grounded holder 200 mm away from the excitation volume of the plasma source) and a 13.56 MHz radio-frequency plasma (pressure 1×10^{-2} mbar, effective power 100 W, sample placed on the driven electrode) were used. "Hard" etching conditions: in the case of radio-frequency plasma, significant self-bias voltages[26] led to ion energies of several 100 eV, which results in a more intense etching effect compared to the mild conditions of the microwave discharge.

Rutherford backscattering spectroscopy measures the energy of particles elastically scattered from the atoms at or near the target sample surface.[27] It thereby can determine the mass of the scattering centers (the atomic nuclei) from the kinematics (using conservation of energy and momentum), and it determines the depth of the scattering centers in the target from the electronic (inelastic) energy loss. The Rutherford backscattering spectroscopy measurements were performed at Forschungszentrum Dresden-Rossendorf (Germany) using the 2 MV van de Graaff accelerator utilizing 1.7 MeV He^+ ions with the detector angle of 170°. Usually, ion beam analysis of polymer layers is challenging since those materials tend to decompose under the analyzing beam even when they are deposited at backings of good thermal conductivity.[28] Therefore, low current densities of <1 nA/mm^2 were used to minimize deterioration of the polymers by the beam. In order to monitor any changes in the layers during the measurement, spectra were obtained in a sequence of exposures, each taken with a fluency as low as 0.1 μC. After each run the beam was shut off, and the data were examined and stored separately. When we observed any significant change in the spectra, the last two spectra were discarded and the former ones were summed up to improve the statistics. Then, a fresh spot was brought to the beam position. The program SIMNRA[29] was used to calculate the depth profiles of sulfur and bromine atoms by fitting the simulated spectra to the Rutherford backscattering spectroscopy data.

Conductive mode atomic force microscopy is a current sensing technique for the local electrical characterizations of samples. Conductive mode atomic force microscopy can be used in either imaging or spectroscopic modes, and both of them were used in this work to probe electrical properties of the pristine and doped PS(Br)-*graft*-P3HT composite films. The 160 nm thick PS(Br)-*graft*-P3HT film on ITO-coated glass for the conductive mode atomic force microscopy measurements was grown from the 60 nm thick photo-cross-linked PS(Br) according to the procedure described above. For comparison, conductive mode atomic force microscopy measurements were also performed on freshly cleaned ITO glass and 60 nm thick photo-cross-linked PS(Br) film. Conductive mode atomic force microscopy measurements were carried out using a NanoScope IV-D3100 (Digital Instruments, Santa Barbara) with conductive Pointprobe EFM N+ silicon tips coated with the Pt−Ir alloy (0.01−0.025 Ω cm) manufactured by Nanosensors (Wetzlar, Germany). Imaging was done at the resonance frequency of 190

Scheme 1. Polycondensation of 2-Bromo-5-chloromagnesio-3-alkylthiophene (1) Initiated by Macromolecular Initiator

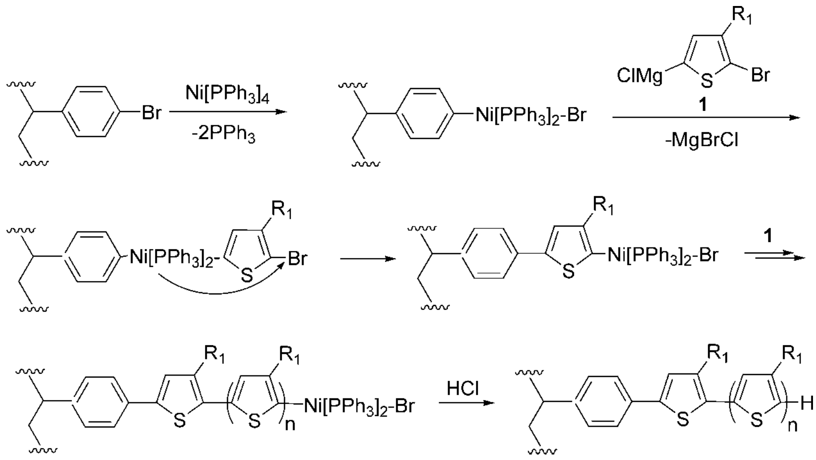


Table 1. Thicknesses of the Photo-Cross-Linked Poly(4-bromostyrene)[a] and Grafted Poly(3-hexylthiophene) Layers, As Measured by Ellipsometry

entry	1	5	3	4	5	6	7
PS(Br) (dry), $h_{PS(Br)}$, nm	1.7	19	33	37	47	84	115
PS(Br) (swollen), $h_{PS(Br)}$, nm	9	40	187	137	144	227	393
P3HT (dry), h_{P3HT}, nm	5	48	77	79	70	101	150
PS(Br)-*graft*-P3HT (swollen), nm[b]	17	98	171	173	288	267	518

[a] All samples contain 2 nm thick poly(glycidyl methacrylate) layer under the poly(4-bromostyrene) layer. [b] These values refer to the overall thickness of the swollen PS(Br)-*graft*-P3HT films.

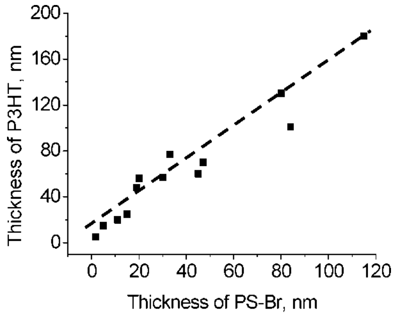


Figure 1. Dependence of the thickness of the poly(3-hexylthiophene) layers on the thickness of the poly(4-bromostyrene) layers.

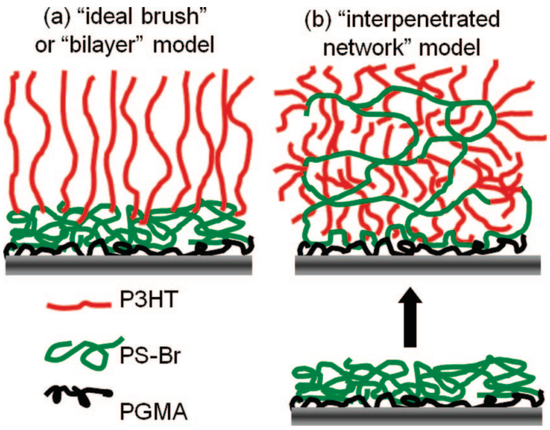
kHz and applied voltage of 1 V. In both cases the conductive tip was grounded, and the potential was applied to the ITO substrate.

UV−vis measurements were carried out using a Perkin-Elmer UV/vis spectrometer Lambda 800.

Results and Discussion

A series of poly(4-bromostyrene), PS(Br), films with the variable thickness from 1 to 200 nm were spin-coated onto Si wafers, precovered by the 2 nm thick poly(glycidyl methacrylate) adhesive layer. PS(Br) films were cross-linked upon a brief irradiation with UV light to ensure their insolubility, while remaining them still swellable in "good" for PS(Br) solvents. Poly(glycidyl methacrylate) reacts with the Si surface upon the annealing and with PS(Br) upon the UV irradiation. The samples were activated with $Ni(PPh_3)_4$ catalyst, and the surface-initiated polycondensation of **1** was performed according to Scheme 1. Results of the ellipsometric thickness measurements for the starting PS(Br) and resulting composite poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) (PS(Br)-*graft*-P3HT) films are given in Table 1 and plotted in Figure 1. The data refer to identical polymerization conditions and correspond to the maximal reachable thickness in each case. Whatever the thickness of the initiating layer, the resulting composite films are very robust against delamination and upon extensive rinsing with various organic solvents in ultrasonic bath and Soxhlet apparatus that unambiguously proves the covalent grafting of P3HT. It was found that in most experiments the films continue to grow substantially only within 3 h and further increase of the reaction time virtually does not change their thickness.

Scheme 2. Schematic Representation of Two Possible Structures for the Poly(3-hexylthiophene) Film Grafted from Photo-Cross-Linked PS−Br Film: (a) "Ideal Brush" or "Bilayer" Model; (b) "Interpenetrated Network" Model



As seen from Figure 1, the thickness of the grafted P3HT layers increases with the thickening of the PS(Br) layers. Thus, the polymerization from the PS(Br) monolayer (1.7 nm) resulted into the grafting of only 5 nm of P3HT, whereas the 115 nm thick PS(Br) layer was transformed into 265 nm thick composite film that corresponds to 150 nm of the grafted P3HT.[30] Furthermore, no saturation in this dependence (Figure 1) was found up to the PS(Br) film thickness of 115 nm. Thicker PS(Br) films were no more stable under the preparative conditions[31] that did not allow further monitoring of this thickness dependence.

These results imply that the polycondensation proceeds not only from the topmost layer of the initiating PS(Br) films, as in classical surface initiated polymerizations into polymer brushes[32] (Scheme 2a), but that also inner layers of the initiating films contribute to the grafting process, as shown in Scheme 2b. The fact that only quite thin P3HT layers are formed from the monolayer of the initiator whatever the polymerization time reflects important termination processes that limit a kinetic chain length (DP_{kin}).[21] According to this assumption, the thickness of the composite PS(Br)-*graft*-P3HT films does not correlate

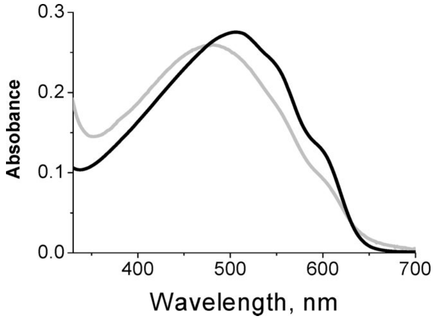


Figure 2. UV spectra of two poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) films prepared under identical conditions demonstrate unittended variations of the growing process that result into different polymerization degree of poly(3-hexylthiophene).

directly with the contour length of the P3HT grafts (that must be very large for thick PS(Br)-*graft*-P3HT films). Instead, the composite films, whatever their thickness, contain rather short P3HT grafts that emanate not only from the topmost PS(Br) chains but also grow from strands located deeply inside the PS(Br) matrix.

The lowest limit of the contour length of the P3HT grafts can be estimated from the results of the polycondensation from the PS(Br) monolayer ($DP_{kin} = 5$ nm/0.38 nm = 13). Assuming that P3HT grafts are tilted or somewhat coiled, the real DP_{kin} might be somewhat higher. Unfortunately, a precise determination of the polymerization degree of P3HT grafts is a challenging task because of impossibility to detach selectively P3HT chains grown from PS(Br).

UV−vis. A crude estimation of the molecular weight of P3HT can be made from UV−vis spectra. It is known that increase of the polymerization degree (DP) of regioregular head-to-tail P3HT results into gradual red shift in the adsorption spectra,[33] especially in "bad" solvent and in a solid state.[34] To calibrate UV−vis absorption versus DP, we synthesized several Ph-terminated P3HT samples of different DPs using $(PPh_3)_2Ni(Ph)Br$, as initiator, according to the previously reported method (Supporting Information, Figure S1).[21] It was found that increase of the DP from 10 to 30[35] results in the red shift of the main absorption band from $\lambda_{max} = 445$ to 518 nm. Unfortunately, virtually no changes in UV−vis spectra of P3HTs are observable when DPs exceed 30 (such as, the spectra of 30-mer and 100-mer are very similar) which limits applicability of this method.

We found that most of the PS(Br)-*graft*-P3HT films obtained by polycondensation from PS(Br) films of different thickness have similar UV−vis spectra with the absorption intensity roughly proportional to their thickness (Supporting Information, Figure S2). Most of the films are violet with the UV−vis spectra fitting to any DPs equal to or higher than 30 (a black line in Figure 2 with $\lambda_{max} = 515$ nm and shoulders at $\lambda = 550$ and 610 nm). It must be noted that even if we keep constant the thickness of the PS(Br) supporting layers and other polymerization parameters due to unintended variations of the reaction conditions, some of the PS(Br)-*graft*-P3HT samples have slightly blue-shifted UV−vis spectra that correspond to DPs < 30 (gray line in Figure 2 that corresponds to DP ~ 20: $\lambda_{max} = 500$ nm and less pronounced shoulders). Importantly, the samples with the blue-shifted adsorption and "violet" one have near the same thickness (if they are grown from the PS(Br) films of the same thickness). Thus, we suggest that the DPs of the P3HT grafts even for the most "violet" samples could not be much higher than 30. This consistent with the kinetic chain length determined previously[21] for the "bulk solution" polycondensation of **1** mediated by the model $(PPh_3)_2Ni(Ph)Br$ initiator under the same reaction conditions, as in the grafting experiments.

Swellability. The grafting of P3HT inside the cross-linked PS(Br) films could be only possible if PS(Br) networks are swellable enough to allow the immobilization of Ni catalyst and penetration of the monomer. Table 1 depicts the swelling behavior for a set of PS(Br) films of variable thickness, before and after the polymerization of P3HT. All the PS(Br) films whatever their thickness are swellable in good solvents (THF and toluene). In most cases the PS(Br)-*graft*-P3HT composite films swell to even higher thicknesses than the parent PS(Br) films that might be attributed to increase of excluded volume interactions inside the networks upon the grafting of P3HT. More importantly, the obtained data suggest that the grafting of P3HT takes place not only from the upper PS(Br) layers but also deeply inside the swollen cross-linked PS(Br) matrix, and even very internal PS(Br) layers are accessible for the polymerization reagents and participate in the grafting process.[36]

X-ray Photoelectron Spectroscopy. To directly investigate the structure and composition of the films, X-ray photoelectron spectroscopy and Rutherford backscattering spectroscopy measurements were undertaken. X-ray photoelectron spectroscopy reveals that 40 nm thick cross-linked PS(Br) film indeed contains C and Br, as major atomic components. The [C]/[Br] ratio is less than the theoretical value (22.7 vs 8) mostly because of contaminations of the surface with carbon and oxygen-reach compounds (Table 2).[37] As expected, the activation of the PS(Br) film with Ni catalyst introduces Ni and P. From the [Br]/[Ni] ratio (6.1) we estimate that ~16% of all Br reacts with the catalyst. The amount of P is reduced factor of 2.5 that might be either due to deviation of the complex structure from the $(PPh_3)_2Ni(Ar)Br$ stoichiometry or due to a presence of some insoluble ligand-free Ni formed due to a decomposition of the Ni complexes. Incorporation of the Ni catalyst is also confirmed by ellipsometry: the treatment of the 40 nm thick PS(Br) films with $Ni(PPh_3)_4$ in the Ar glovebox followed by washing of the excess of $Ni(PPh_3)_4$ with dry toluene results into 61 nm thick film. A rather significant amount of S ([C]/[S] ratio of 21.4) and no Ni and P contains the sample after the grafting of P3HT (overall thickness increases from 40 to 130 nm). Importantly, a high content of Br ([S]/[Br] = 4.9) could not be explained by the P3HT termination, even if all P3HT chains are terminated by Br atoms (the observed [Br]/[S] = 1/5 ratio corresponds to DP = 5 and to the contour length of 0.38 nm × 5 = 1.9 nm, which is much less that the penetration depth of X-rays in this experiment, e.g., of ~8 nm). Thus, the high content of Br reflects that significant amount of PS(Br) is still remained even in the upper layer of the PS(Br)-*graft*-P3HT composite film.

To reveal the PS(Br)-*graft*-P3HT films composition in deeper layers than the information depth of X-ray photoelectron spectroscopy method, the samples were etched with Ar plasma. To diminish the sample damage, the etching was performed in relatively mild conditions with the rate of about 0.6 nm/min. After the removal of the upper 20 nm from the 130 nm thick composite film (40 nm of PS(Br) + 90 nm of P3HT) with Ar plasma, the X-ray photoelectron spectroscopy measurements were conducted. They reveal lowering of the oxygen content compared to the sample before the etching. We found the increase of S content compared to the sample before the etching. Even more important, the content of Br atoms is also increased substantially, proving that bromine reflects here not the P3HT chains termination, but the presence of PS(Br). Thus, these experiments further confirm the validity of the "interpenetrating" model and decline the "bilayer" (or "brush") structure (Scheme 2). Unfortunately, attempts to etch deeper the composite films without significant damage of their surface composition by prolonged exposure to Ar plasma were failed: no S or Br was found by X-ray photoelectron spectroscopy in such extensively

Table 2. Elemental Compositions of Polymer Surfaces after Different Transformation Steps of the Grafting Process (Samples 1−3) and after the Ar-Plasma Etchings (Samples 4 and 5), As Derived from X-ray Photoelectron Spectra

	atomic concentration (%)						atomic ratio		
	C 1s	O 1s	P 2p	Ni $2p_{3/2}$	Br 3d	S 2p	[C]:[Br]	[C]:[S]	others
1. PS(Br)	84.9	10.93	0.43		3.74		22.7		
2. PS(Br)/Ni(PPh_3)$_2$	81.27	11.23	0.66	0.82	5.02		16.19		[P]:[Ni]: 0.80 [Br]:[Ni]: 6.1
3. PS(Br)/P3HT	86.23	8.91			0.82	4.03	105.16	21.40	[S]:[Br]: 4.91
4. PS(Br)/P3HT etched “mild”	89.36	5.13			0.88	4.63	101.54	19.30	[S]:[Br]: 5.26
5. PS(Br)/P3HT etched “hard	33.13	66.02			0.85		38.98		

etched samples along with appearance of O, F, and Na and clear signs of the polymer degradation (Supporting Information).

Rutherford backscattering spectroscopy is ideally suited for obtaining elemental depth profiles of heavy elements (such as S and Br) in a matrix of lighter elements (such as C) with the resolution up to 10 nm.[38] As such, the “intermixed” and “bilayer” models for the structure of the PS(Br)-*graft*-P3HT composite films must be clearly distinguishable with this technique. According to the “intermixed” model, S and Br must be distributed more or less homogeneously in the films, whereas the “bilayer” model assumes depth segregation of S and Br with S located atop of Br. A 140 nm thick PS(Br)-*graft*-P3HT composite film similar to one used in XPS experiments was prepared by the grafting of P3HT from 50 nm thick cross-linked PS(Br) layer. Its Rutherford backscattering spectroscopy spectra is shown in Figure 3a,b. The horizontal scale shows the kinetic energy of the backscattered helium ions. Different species are readily identified by their position along abscissa and are indicated on the plot. The sulfur the bromine peaks confirm the presence of the P3HT and PS(Br), respectively. The signals arising from carbon and hydrogen in the polymer and the Si substrate, both of which occur at lower energy and are ignored in the further analysis. Any incorrect C/H ratio has practically no influence on the Br/C and the S/C atomic ratios. The layer thickness measured by Rutherford backscattering spectroscopy was found to be 2800 × 10 × 15 atoms/cm^2. The concentration of S is 7% and Br is 4.5% in the brush model and was estimated by comparison of the signal intensities and standard *k*-factor analysis. The quite intense Br signal suggests that not all bromine atoms in the PS(Br) layer are consumed during the grafting process. This corroborates with X-ray photoelectron spectroscopy data showing that only ∼16% of Br atoms react with Ni(PPh_3)$_4$.

The thick distribution of component S and Br proved that the P3HT and PS(Br) components are *intermixed* in this sample. Figure 3b presents the SIMNRA simulation for the same PS(Br)-*graft*-P3HT, but assuming the “bilayer” model. Clearly, the Rutherford backscattering spectroscopy spectra could not be fitted satisfactorily by this model.

For comparison, the Rutherford backscattering spectroscopy measurements and simulations were performed for the reference sample with the predefined bilayer structure (Figure 3c,d). To prepare the reference sample, 2 nm of PGMS and 50 nm of PS(Br) were deposited by spin-coating and cross-linked by UV irradiation for 1 min. Afterward, 90 nm of regioregular HT P3HT was spin-coated atop. The best fit of the Rutherford backscattering spectroscopy measurements here is obtained using the “bilayer” model. The amounts of each component in the “bilayer” model are the following: on the top layer, the S is 7% and the Br is 0.2% of the coated P3HT, and on the bottom, the Br is 8% of the PS(Br). The thickness of the top layer is 830 × 10 × 15 atoms/cm^2, and the thickness of the bottom layer is 420 × 10 × 15 atoms/cm^2. As expected, no signal of sulfur was found in the bottom layer, confirming the validity of the method.

Conductive Mode Atomic Force Microscopy Measurements[39]. It was previously shown that the PS(Br)-*graft*-P3HT films display rather good lateral direct current (dc) conductivity in their doped state (∼2 S/cm).[21] To probe local electrical properties of the films in the perpendicular to the surface direction, the conductive mode atomic force microscopy measurements were performed in tapping and contact modes. By

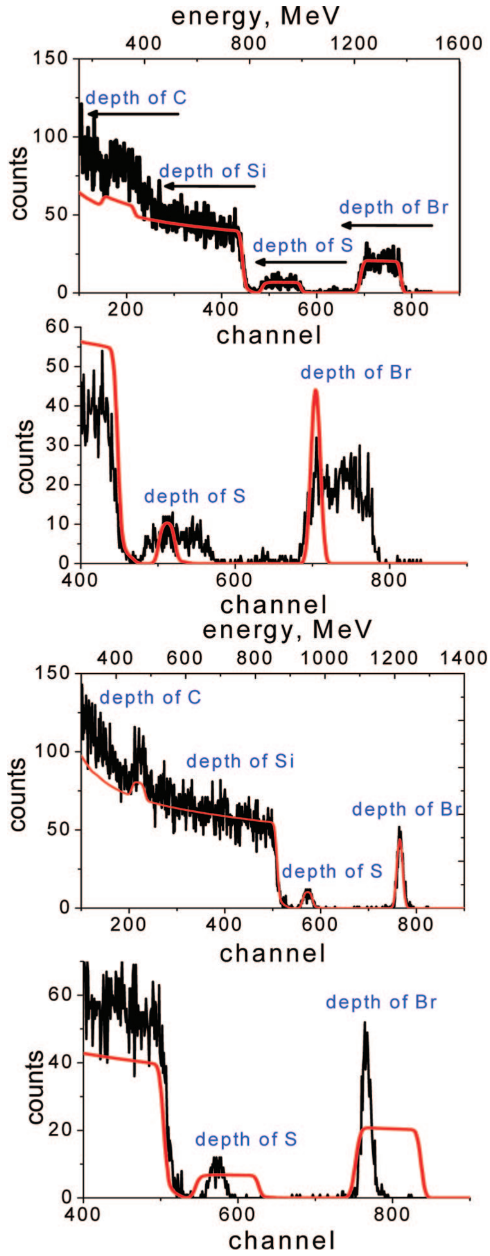


Figure 3. Rutherford backscattering spectra (black line) and SIMNRA simulations (red line) of the poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) sample (a and b) and of the reference “bilayer” sample with poly(3-hexylthiophene) film spin-coated atop of the cross-linked poly(4-bromostyrene) film (c and d). SIMNRA simulations were performed for both samples assuming either the “intermixed” or the “bilayer” structures. The best fit was achieved for the poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) sample by the “intermixed” model and for the reference “bilayer” poly(3-hexylthiophene) spin-coated atop of poly(4-bromostyrene) sample by the “bilayer” model.

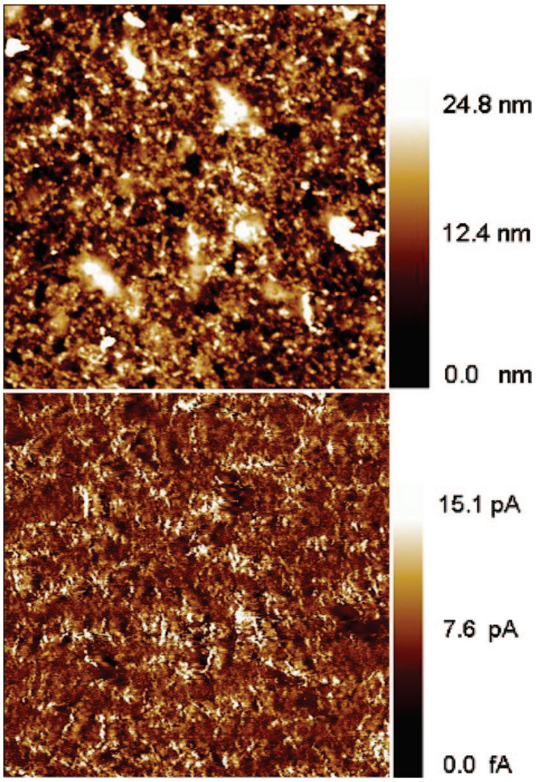


Figure 4. 4 × 4 square μm topography (a) and conductive mode atomic force microscopy current images (b) of the 160 nm thick poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) film grown from 60 nm thick cross-linked PS−Br (60 nm) deposited on ITO glass.

maintaining a constant force between tip and sample, simultaneous topographic and current images were generated, enabling the direct correlation of the local topography with electrical properties. As seen from Figure 4a, the film displays quite smooth morphology with a size of features (up to 20 nm) much less than the film thickness (∼160 nm). The current image (Figure 4a) is also quite homogeneous. To acquire $I-V$ characteristics of the PS(Br)-*graft*-P3HT film in the perpendicular to the surface plan direction, the conductive mode atomic force microscopy measurements were performed in contact mode, with a preset pressure between the tip and the sample. The measurements were performed at least in seven points for each of the samples investigated, and the representative data are shown in Figure 5. The measurements of the conductivity of the freshly cleaned ITO glass and of the photo-cross-linked 160 nm thick PS(Br) film reference samples were performed for comparison.

As expected for a good conductor, the ITO-coated glass displays an ohmic-like $I-V$ behavior and has the lowest resistance (R) among the samples investigated (Figure 5a). The PS(Br) film is an insulator within the voltage diapason applied (up to 5 V) (Figure 5b). $I-V$ curves for the pristine and FeCI$_3$-doped PS(Br)-*graft*-P3HT films exhibit semiconductor-like characteristics. The pristine PS(Br)-*graft*-P3HT show relatively high R (∼50 Gohm, Figure 5c), and the R value drops 5 orders of magnitude after the doping (R ∼ 1 Mohm, Figure 5d).

The conductivity, σ, was roughly estimated assuming that the contact tip/sample area is given by the size of the tip (radius of ∼70 nm).[40] R of the samples was estimated from the inverse slope of the $I-V$ curve. When the $I-V$ curve is not linear, the slope of the curve was estimated from the linear fit of the curve. Thus, the conductivities of the film in the pristine and in the doped states were found to be of ∼10^{-5} and ∼1 S/cm, respectively, which is close to the lateral conductivity for these samples. Such results further confirm that the developed procedure for the P3HT grafting converts the insulating PS(Br) films into semiconductive PS(Br)-*graft*-P3HT one. Furthermore, the fact that the films are conductive in the perpendicular to the surface direction corroborates the assumption that the grafting of P3HT occurs inside the PS(Br) matrix.[41]

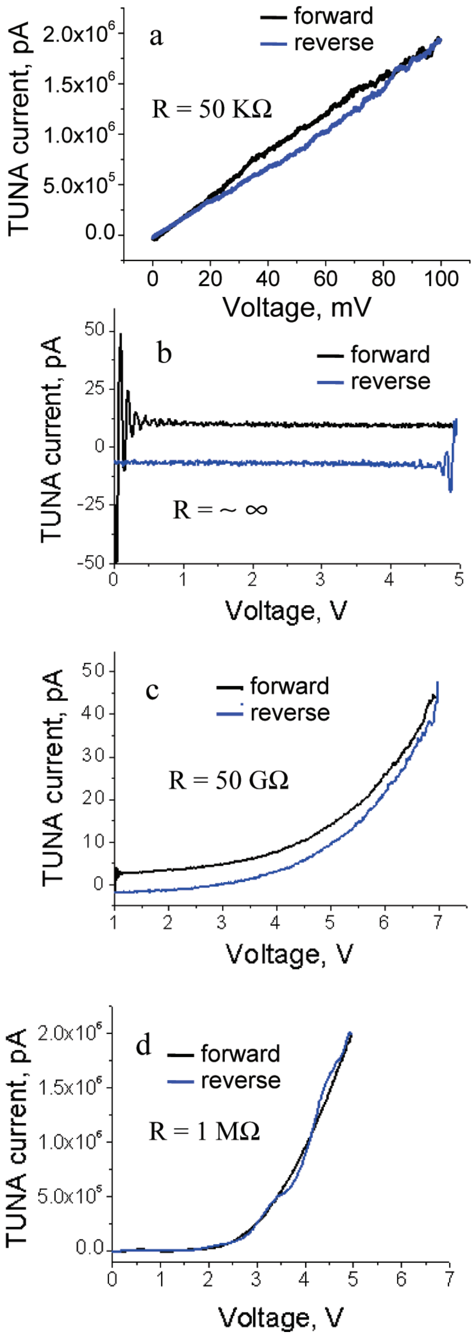


Figure 5. Representative $I-V$ characteristics collected by conductive mode atomic force microscopy for four different samples: ITO-coated glass substrate (a); 60 nm thick poly(4-bromostyrene) film atop of the ITO-coated glass substrate (b); 160 nm thick poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) film atop of the ITO-coated glass substrate (c); the same film as in (c), but after the doping with FeCl$_3$ (d).

Conclusions

Only a marginal grafting of poly(3-hexylthiophene) is observed if the surface-initiated Kumada catalyst-transfer polycondensation is performed from thin poly(4-bromostyrene) layers because of significant chain-termination processes. However, much thicker poly(3-hexylthiophene) films (up to 150 nm) can be grafted from thick (e.g., 100 nm), highly swellable poly(4-bromostyrene) films. The detailed investigation of the grafting process and direct study of the structure of the resulting composite poly(4-bromostyrene)-*graft*-poly(3-hexylthiophene) films by ellipsometry, X-ray photoelectron spectroscopy, Rutherford backscattering spectroscopy, and conductive mode atomic force microscopy techniques allow to conclude that the grafting proceeds not only from the topmost layer of poly(4-bromostyrene) film, but also takes place deeply inside the poly(4-bromostyrene) matrix (Scheme 2b). The process results into a kind of interpenetrated network in which relatively short (∼10 nm) poly(3-hexylthiophene) grafts emanate from long and cross-linked poly(4-bromostyrene) chains. The films show good stability against delamination, high electrical conductivity in the doped state, and high swellability that might be exploited for construction of fully "plastic" electronic devices and sensors.

Acknowledgment. We thank Ulrich Oertel and Bettina Pilch for the UV−vis measurements. Financial support was provided by the Deutsche Forschungsgemeinschaft (STA 324/25-1 and SFB 287-B1).

Supporting Information Available: X-ray photoelectron spectroscopy, UV−vis data, and synthesis of poly(4-bromostyrene). This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) In all cases "the thickness of the grafted P3HT" means the increase of the film thickness after the polymerization of P3HT; thus, PS(Br) film with the initial thickness of 115 nm becomes 115 + 150 = 265 nm thick, as deduced by ellipsometry.

(31) They detached from Si support during the rinsing step resulting into PS(Br)-*graft*-P3HT free-standing films.

(32) Surface-initiated polymerizations of polyolefins usually do not require thick layers of initiators; living surface-initiated polymerizations show linear dependence of the thickness of the grafted polymer layers on the polymerization time.

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(36) For example, comparing entries 5 and 6 in Table 1 and assuming the polymerization conditions in these two experiments to be identical, we can estimate the contribution of deepest layers of the PS(Br) of the sample 6 into the grafting process. Since the 84 nm thick PS(Br) film grafts 101 nm of P3HT (entry 5), whereas the 115 nm thick sample 6 gives 150 nm thick P3HT film, the contribution of the additional 31 nm thick PS(Br) in the sample 6 (115−84 nm) is responsible for the grafting of additional 39 nm of P3HT.

(37) 10.7% of O is found in PS(Br) sample. We cannot rule out possibility of oxidation of PS(Br) during UV cross-linking; however, this unlikely could explain the major part of the oxygen found, since even the sample after P3HT polymerization contains about 9% of O.

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MA800889C