Supporting Information to the manuscript:

Grafting of Poly(3-alkylthiophenes) from Poly(-4-bromostyrene) Films by Kumada Catalyst-Transfer Polycondensation (CTP): a Structure of Composite Films

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1. XPS Report

Spectrometer: AXIS ULTRA (Kratos Analytical, England)
                       X-Ray-source: Mono-Al K$\alpha_{1,2}$, power of the x-ray source: 300 W at 20 mA, analyser: pass energy 160 eV (survey spectra) and 20 eV (high-resolved spectra), charge compensation switched on

Samples investigated:
① sample 1: 40 nm PS-Br on silicon wafer,
② sample 2: 40 nm PS-Br treated by Ni(TPP)$_4$ catalyst,
③ sample 3: 40 nm PS-Br + grafting-from of 90 nm P3HT, not etched
④ sample 4: 40 nm PS-Br + grafting-from of 90nm P3HT, etched 20 nm in "mild" conditions
⑤ sample 5: 40 nm PS-Br + grafting-from of 90nm P3HT, etched 30 nm in "hard" conditions

Take-off angle Θ: (angle between surface normal and electron-optical axis of the spectrometer)
                       Θ = 0° ≙ maximum information depth ID ≈ 8   nm[1,2]

Charge compensation
All spectra were formally charge-compensated using the C 1s peak of the saturated hydrocarbons (BE = 285.00 eV)[3] or the unsaturated hydrocarbons of the phenyl ring (BE = 284.7 eV)[3] as reference. Negative values of charge compensation indicate an overcompensation guaranteeing unadulterated peak shapes.

	①	②	③
survey spectrum	-1.616 eV		
C 1s spectrum	-2.085 eV		
S 2p spectrum	-2.085 eV		

	④	⑤
survey spectrum	-3.35 eV	-2.15 eV
C 1s spectrum	-3.772 eV	-2.377 eV

1   Briggs, D: Characterization of surfaces, Pergamon, Oxford, 1989
2   Seah, M.P.; Dench, W.A.: Surface Interface Analysis, VOL 1 (1979), S. 2
3   Beamson, G.; Briggs, D: High resolution of organic polymers, The Sienta ESCA 300 Database, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapur, ISBN 0-471-93592-1 (1992).

S 2p spectrum	-3.772 eV	-2.377 eV

Survey spectra

The sample surfaces showed the following elements:

carbon (6):   as C 1s peak,

oxygen (8):   as O 1s, O 2s, O KL1 = O $KL_{23}L_{23}$, O KL2 = O KL_1L_{23} and O KL3 = O KL_1L_1 peaks

fluorine (9):   as F 1s and FKL1 = F $KL_{23}L_{23}$ peaks (only in sample ⑤),

aluminium (13):   as Al $2p_{3/2}$, Al $2p_{1/2}$ and Al 2s peaks (only in sample ⑤),

silicon (14):   as Si $2p_{3/2}$, Si $2p_{1/2}$ and Si 2s peaks (only in sample ② and ⑤),

phosphorus (15)   as P $2p_{3/2}$, P $2p_{1/2}$ and P 2s peaks (only in sample ②),

sulfur (16):   as S $2p_{3/2}$, S $2p_{1/2}$ and S 2s peaks (not in sample ①, ② and ⑤),

iron (26):   as Fe $2p_{3/2}$, Fe $2p_{1/2}$, Fe $3p_{3/2}$, Fe $3p_{1/2}$ and Fe 3s peaks (only in sample ①)

nickel (28):   as Ni $2p_{3/2}$, Ni $2p_{1/2}$, Ni LM1 = Ni $L_3M_{45}M_{45}$, Ni LM2 = Ni $L_3M_{23}M_{45}(^1P)$, Ni LM3 = Ni $L_3M_{23}M_{45}(^3P)$ + Ni $L_3M_{23}M_{45}(^1P)$ and Ni LM4 = Ni $L_2M_{23}M_{23}$ + Ni $L_3M_{23}M_{23}$ peaks,

bromine (35):   als Br 3s, Br $3p_{3/2}$, Br $3p_{1/2}$, Br $3d_{5/2}$, Br $3d_{3/2}$, Br 4s, Br $4d_{5/2}$ and Br $4d_{3/2}$ peaks.

Quantification

To determine elemental ratios normalized peak areas were calculated from peak areas (`Raw Area [CPS]`) of survey spectra according to eq. 1 respecting sensitivity factors[4] (`RSF`) and spectrometer's transmission function (`Tx.Function`):

$$\mathtt{Norm\,Area} = \frac{\mathtt{Raw\,Area}}{\mathtt{RSF} \cdot \mathtt{Tx.Function}}$$
(1)

(CPS = count per second; (BE = binding energy [eV])

	①	②	③	④	⑤
[N]:[C]l$_{spec}$	–	–	–	–	–
[O]:[C]l$_{spec}$	0.007	0.126	0.103	0.058	1.993
[F]:[C]l$_{spec}$	–	–	–	–	0.006
[Na]:[C]l$_{spec}$	–	–	–	–	–
[Al]:[C]l$_{spec}$	–	–	–	–	0.451
[Si]:[C]l$_{spec}$	–	0.005	–	–	–
[P]:[C]l$_{spec}$	–	0.005	–	–	–
[S]:[C]l$_{spec}$	–	–	0.047	0.058	–
[Fe]:[C]l$_{spec}$	–	0.004	–	–	–
[Ni]:[C]l$_{spec}$	–	–	–	–	–
[Br]:[C]l$_{spec}$	0.091$^{a)}$	0.044	0.009	0.011	0.025

a) The stoichiometric ratio is [Br]:[C]l$_{spec}$ = 0.125.

C 1s spectrum of sample ①

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[4] experimentelly determined for our spectrometer KRATOS AXIS ULTRA.

The C 1s spectrum of sample ① confirms the C 1s spectrum expected for poly(4-bromostyrene)[5]. The spectrum was deconvoluted into three component peaks *A*, *B* and *C* showing the carbon atoms of the phenyl ring (*A*), the saturated hydrocarbons (CH–CH$_2$, *B*) of the polymer backbone and the carbon bond to bromine (C–Br, *C*). The intensity ratio [*C*]:[*A*] = 0.2 excellently agrees with the given stoichiometry. An excess of saturated hydrocarbons appearing from surface contaminations was observed.

The spectrum also shows intensive *shake-up* peaks resulting from $\pi \rightarrow \pi^*$ electron transitions. These transitions occurring in the conjugated π-orbitals of the phenyl rings. The share area of the *shake-up* is [*shake-up*]:[*C 1s*] = 0.056.

C 1s spectrum of sample ②
The C 1s spectrum of sample ② is similar to the spectrum of sample ①. It was also deconvoluted into three component peaks *A*, *B* and *C* representing the binding species explained above. However, the share area of component peak *C* (showing C–Br bonds) was decreased and component peak *A* showed a higher intensity. This can be explained by the presence of an additional number of phenyl rings from polystyrene. The *shake-up* area is slightly lowered [*shake-up*]:[*C 1s*] = 0.034.

C 1s spectrum of sample ③
Beside the three component peaks explained above, the spectrum shows two additional component peaks appearing from oxidized carbon species. Component peak *D* indicates C–O bonds of ether (C–O–C) or alcoholic C–OH groups. Component peak *D* could show keto groups (C=O). Surprisingly, the spectrum does not show a pronounced *shake-up* regions. That indicates that the number of conjugated π-orbitals is decreased. Such a phenomenon is usually observed if oxidation reactions (e.g. plasma treatments) were carried out on polyenes or polyarenes or polyarenes were soiled by surface contaminations.

C 1s spectra of sample ④
In this spectrum the component peak *A* shows unsaturated as well as saturated hydrocarbons. It was set as reference with a binding energy of BE = 284.7 eV. The second component peaks *B* mainly shows C–S and some C–Br groups. Compared to the corresponding wide scan spectrum the intensity of component peak *B* is the double of the [S]:[C]$_{spec}$ ratio plus the [Br]:[C]$_{spec}$ ratio. It can be concluded that sulfur bridges two carbon atom like a thioether (C–S–C). The two other component peaks can be explained by oxidized carbon species as described for sample ③. A slight *shake-up* region arises at BE $\approx$ 293 eV.

C 1s spectra of sample ⑤
The C 1s spectrum shows a completely decomposed polymer film. Rests of the poly(4-bromostyrene) were identified by the component peak *Ph*. The main component peak *A* shows saturated hydrocarbons can be considered as degradation product. The three intensive component peaks *B*, *C* and *E* show that the sample surface is highly functionalized by oxygen containing groups. According their binding energies they can be assigned to ether C–O–C or alcoholic C–OH groups (in the case of ester presence also the alcohol-side carbon O=C–O–C, component peak *B*), keto groups (C=O, component peak *C*) and carbonic acids O=C–OH (or ester groups, O=C–O–C, component peak *E*).

5   Beamson, G.; Briggs, D.: High resolution of organic polymers, The Sienta ESCA 300 Database, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapur, ISBN 0-471-93592-1 (1992), pp 274-275.

S 2p spectra

S 2p spectra are composed by the S $2p_{3/2}$ and S $2p_{1/2}$ peaks. The two peaks have a coupling constant $\Delta BE = |BE(S\ 2p_{3/2}) - BE(S\ 2p_{1/2})| = 1.18$ eV. The intensity ratio is given by $[S\ 2p_{3/2}]:[S\ 2p_{1/2}] = 2:1$.

The S 2p spectrum of sample ④ shows only one binding state of sulfur. The binding energy found is typical for elemental sulfur and organic sulfides (e.g. mercapto and thioether groups, cysteine and $C–\underline{S}–(S)_{n-1}–C$ bonds).

The S 2p spectra ③ and ⑤ also show traces of a second sulfur species. In sample ③ the peaks of the second sulfur species (*C*) is slightly shifted to higher binding energies, but their binding energies do not correspond to binding energies indication oxygen as binding partner. The shift to lower binding energies in sample ⑤ could indicate inorganic sulfides (e.g. NiS, but in literature the binding energy of NiS is lower $BE[Ni\underline{S}] = 162.2$ eV[6])
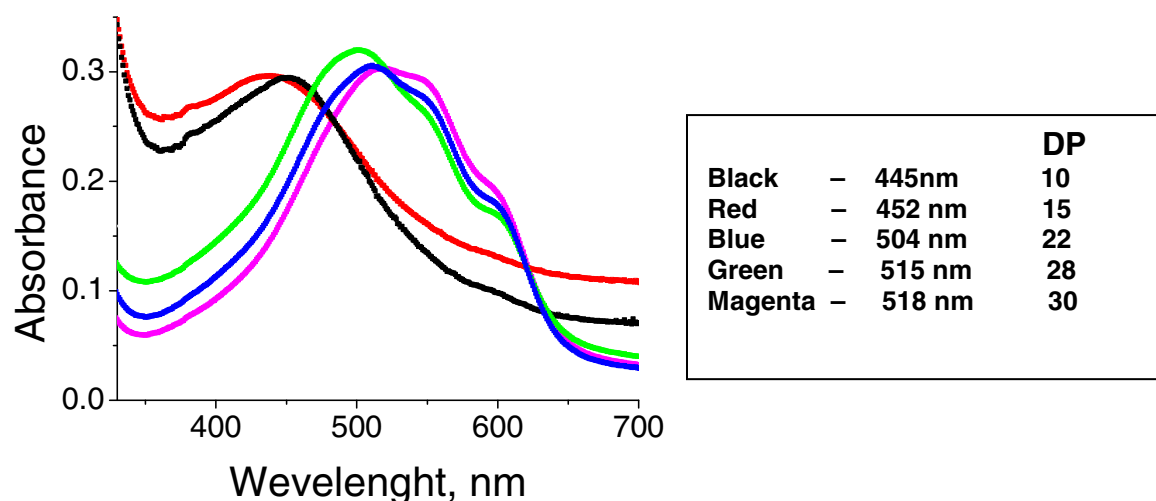
UV-vis data

Figure S1. UV-spectra of P3HT samples of different DP (absolute values, as determined by NMR[1]H) prepared by spin-coating onto PGMA-coated (2nm) glasss slides.

6   Ng, K.T.; Hercules, D.M.: J. Phys. Chem.80 (1976) p. 2095
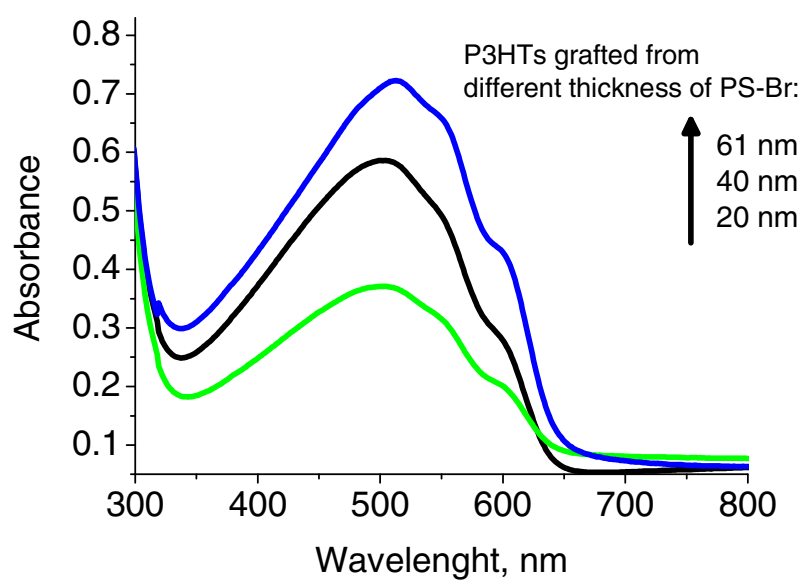   Dickingson, T.; Povey, A.F.; Sherwood, P.M.A.: J. Chem. Soc. Faraday Trans. I 72 (1977) p. 686.

Figure S2. UV-spectra of grafted P3HT brushes from different thicknesses of PS-Br

Poly(4-bromostyrene), PS(Br)

4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) was prepared by the method reported previously (Miyazawa, T.; Endo, T.; Shiihashi, S.; Okawara, M. *J. Org. Chem.* 1985, *50*, 1332.) Benzoyl peroxide was purified by precipitation from chloroform into methanol and then crystallized in methanol at 0°C. Commercial grade p-bromostyrene was washed with aqueous alkaline solution and water, and distilled over calcium hydride. 0.75 mL (1.05 g, 5.74 mmol) of p-bromostyrene, 18 mg (0.0743 mmol) of benzoyl peroxide, and 28 mg (0.151 mmol) of MTEMPO were placed in an ampule. After degassing the content, the ampule was sealed in vacuo. The polymerization was carried out at first for 3.5 h at 95°C and then continued for another 48 h at 125°C. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, evaporated under reduced pressure, and finally dried in vacuo for several hours to give the polymeric product. It was purified by precipitation of concentrated solution in dichloromethane into methanol, collected by filtration and dried. Yield – 670 mg, 64%). GPC data: M_n= 51000 g/mol, PDI=2.05.