A Facile Route to Electronically Conductive Polyelectrolyte Brushes as Platforms of Molecular Wires

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Supplementary Information

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Materials and methods

Materials. 2-hydroxy-5-iodopyridine (97%), triethylamine (TEA >99%), diethylthiocarbamic acid diethylammonium salt (97%), chloroform-d (99.8% atom D) and iodine (≥99.8%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh)₃), copper(I) iodide (for synthesis), trimethylsilylacetylene (TMSA for synthesis), tetrahydrofuran (p.a), n-hexane (p.a), silica gel 60 (230-400 mesh) for column chromatography were all obtained from Merck (Whitehouse Station, NJ, USA). Iodoethan (for synthesis), ammonium chloride (99.5%), magnesium sulfate (anhydrous 99.5%) were purchased from Alfa Aesar (Ward Hill, MA, USA). (P-chloromethyl) phenyltrimetoxysilane (95%) was puchased from ABCR (Karlsruhe, Germany). Toluene (p.a.), dimethylformamide (p.a.), ethyl acetate (p.a.) and dichloromethane (p.a) were purchased from Chempur (Piekary Slaskie, Poland). Ammonia solution (25% p.a.) was obtained from POCH S. A. (Gliwice, Poland). Hydrogen peroxide (30% p.a.) was purchased from Stanlab (Lublin, Poland). They were all used as received. Methacryloyl chloride (97%, Sigma Aldrich) was distilled before usage. Nisopropylacrylamide (NIPAM, monomer, Sigma Aldrich) was purified by recrystalization in hexane. ITO glass with the ITO layer thickness of 150 nm (resistance $12\Omega/sq$.) and overall plate thickness 1.1 mm was purchased from VisionTek System LTD (Cheshire, United Kingdom).

Methods. The contact angle measurements were recorded on OEG Surftens Universal apparatus. NMR spectra were measured on Bruker AMX 500 spectrometer. FTIR spectrum of the monomer was recorded using Bruker Equinox 55 spectrometer equipped with ATR (attenuated total reflectance) accessory. FTIR spectra of polymer brushes and monolayers on ITO were recorded using Nicolet iS10 FT-IR spectrometer with grazing-angle reflectance accessory (84° angle was used for all the measurements). Reflectance UV-VIS spectra of the brushes were measured using Ocean Optics USB2000-VIS-NIR spectrophotometer equipped with an integrating sphere. The UV-VIS spectrum of the solution of the synthesized monomer was measured on Varian Cary 50 UV-VIS spectrometer in a quartz cuvette. The XPS spectra of the brushes were measured using Versa Probe II (PHI Electronics) spectrometer. Ellipsometric measurements were performed on M-2000U (J.A. Woollam Co.) spectroscopic ellipsometer working in 250–1000 nm spectral range. The thickness of the studied layer on silicon oxide was

determined by fitting the measured data using classical Cauchy model (refractive index, k, for the organic layer was assumed to be equal to 1.45). Atomic Force Microscope (AFM) images were obtained with Dimension Icon AFM (Bruker, Santa Barbara, CA) working in the PeakForce Tapping (PFT) and QNM® mode with standard silicon cantilevers for measurements in the air (nominal spring constant of 0.4 N/m). PeakForce TUNA mode (tunneling AFM) was used for conductivity imaging (bias voltage equal to 25 mV) and collecting of I-U curves. The silicon probes coated with Pt/Ir layers on both sides (with nominal spring constant of 0.4 N/m and radius of curvature of 25 nm) were used for all the electrical measurements. I-U plots for all samples were obtained under the same conditions using ramp mode with low setpoint value (external load was set close to zero, below 10 pN) and the voltage applied between the tip and the sample surface that was ramped in the range -150 mV to +150 mV. The plots were recorded in at least 500 random points for each sample.

The photoiniferter-mediated polymerization was conducted in the Rayonet photoreactor equipped with 8W UV lamps with maximum emission at 300 nm (Luzchem LZC-UVB). The actual total power of the lamps used in a given experiment is presented in Table 1.

Thickness of the brushes was determined using the AFM "scratch method". Standard tapping mode silicon tips with nominal spring constant of 40 N/m working in contact mode were used to make a scratch in the brush by applying high external load (high deflection setpoint value). The same tip working in the tapping mode was then used to take a surface topography image. Depth of the formed scratch was taken as the thickness of the brush coating. The procedure was repeated several times for a given sample and the obtained values were averaged.

Experimental procedures

Synthesis of 5-[2-(trimethylsilyl)ethynyl]pyridin-2-yl 2-methylprop-2-enoate (MTEP) monomer

In the first step of the synthesis of MTEP monomer (see scheme S1), 5-[2-(trimethylsilyl)ethynyl]pyridin-2-ol precursor was synthesized using the previously described procedure.¹ Briefly, 2-hydroxy-5-iodopyridine (1.5 g, 6.8 mmol) (1), copper(I)

iodide (0.100 g, 0.52 mmol), and PdCl₂(PPh₃)₂ (0.189 g, 0.12 mmol) were mixed in a conical flask equipped with a magnetic stirring bar. Triethylamine (30 ml) and tetrahydrofuran (110 ml) were then added to the reaction mixture and the flask was closed with a rubber septum. Trimethylsilylacetylene (3 ml, 21.2 mmol) was added dropwise and the reaction mixture was stirred at 45°C overnight under argon atmosphere. The reaction was quenched with a saturated solution of NH₄Cl (50 ml) and the organic layer was diluted with hexane and subsequently washed with water (2x30 ml) and saturated NH₄Cl (twice 30 ml). The combined aqueous layers were extracted with hexane (twice 30 ml) and CH₂Cl₂ (twice 30 ml). The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed in rotary evaporator. The crude product was purified by SiO₂ column chromatography using the mixture of ethyl acetate and hexane (first 10/90, and then 50/50 v/v). After removing the solvent a slightly colored solid was obtained. 1 H NMR (500 MHz, CDCl₃, δ): 12.82 (s, 1H, OH), 7.53 (d, 1H, CH), 7.47 (dd, 1H, CH), 6.50 (d, 1H, CH), 0.22 (s, 9H, CH₃-Si). ¹³C NMR (500 MHz, CDCl₃, δ): 163.9 (C-OH), 144.1 (CH), 138.6 (CH), 120.2 (CH), 103.7 (C=C), 100.1 (C), 95.3 (C-Si(CH₃)₃), -0.11 (CH₃-Si). In the second step of the synthesis the following procedure was used. The product of the first synthetic step (0.92 g, 4.8 mmol) was mixed with triethylamine (3.5 ml, 24 mmol) and dichloromethane (50 ml) in a conical flask equipped with a magnetic stirring bar. The reaction flask was closed with a rubber septum, placed in an ice bath and purged with argon. Methacryloyl chloride (0.46 ml, 4.8 mmol) was added dropwise and the reaction mixture was stirred at 0°C for 0.5 h and then at room temperature for the next 4h. Upon completion the reaction mixture was washed with brine (three times 30 ml). The combined aqueous layers were extracted with dichloromethane (twice 30 ml). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed in a rotary evaporator. The crude product was purified by SiO₂ column chromatography (preadsorption to the stationary phase was applied) using 2.5% ethyl acetate in hexane. Removing the solvent in rotary evaporator resulted in a slightly colored solid. ¹H NMR (Fig. S1) (500 MHz, CDCl₃, δ): 8.48 (s, 1H, CH), 7.83 (dd, 1H, CH), 7.07 (d, 1H, CH), 6.41 (q, 1H, =CH), 5.81 (q, 1H, =CH), 2.06 (t, 3H,C-CH₃), 0.26 (s, 9H, CH₃-Si). 13 C NMR (Fig. S2) (500 MHz, CDCl₃, δ): 165.1 (C-OH), 157.2 (COOR), 151.6 (CH), 142.3 (CH), 135.3 (C-CH₃), 128.4 (C=CH₂), 118.7 (CH), 115.9 (C=C), 100.5 (C), 98.4 (C-Si(CH₃)₃), 18.2 (CH₃), -0.11 (CH₃-Si). IR (Fig. S3): 3100- 3040 cm⁻¹ (w, v_s (C-H), alkenes/aromatic), 2963- 2863 cm⁻¹ (m, v_s (C-H), alkane), 2163 cm⁻¹ (m, v_s C=C), 1740 cm⁻¹ (s, v_s (C=O), carbonyl), 1635 cm⁻¹ (w, v_s (C=C), alkene), 1588, 1566 cm⁻¹ (m, v_s (C=C), aromatic ring), 1475 cm⁻¹ (s, v_{def} (CH₃, CH₂)), 1220 cm⁻¹ (s, v_s (Si-CH₃)).



Scheme S1. Scheme of the synthesis of MTEP monomer.

Preparation of the self-assembled monolayer (SAM) of photoiniferter on ITO surface

The self-assembled monolayer (SAM) containing photoiniferter head groups was synthesized on the surface of ITO in two steps presented in Scheme S2. In the first synthetic step the ITO plate was cleaned in the mixture of 30% hydrogen peroxide, 25% ammonia and water (v:v:v, 1:1:1) for 2h at room temperature. Afterwards, ITO plate was rinsed with copious amount of water, tetrahydrofuran and toluene and dried in the stream of argon. The clean substrate was immersed in 5ml of toluene in a glass vial stopped with a rubber septum. The reaction mixture was purged with argon and subsequently 5.5 µl of (chloromethyl)phenyltrimethoxysilane was added dropwise. The reaction mixture was left to react at room temperature overnight under argon atmosphere. Upon completion the ITO plate was rinsed with copious amount of toluene and THF and additionally immersed in clean toluene and THF bubbled by argon and dried in the stream of argon. In the second step, the ITO plate with the obtained monolayer was immersed in the solution of diethylammonium diethyldithiocarbamate in THF (5 mM) and the reaction mixture was purged with argon and left to react at room temperature overnight. Afterwards, the sample was rinsed with copious amount of the following solvents: THF, water, THF (again), toluene and bubbled in using argon. It was then sonicated for 20 min. in fresh toluene solvent, rinsed with copious amount of toluene and THF and finally dried in the stream of argon. After each synthetic step the sample was characterized by grazing-angle reflectance FTIR (Fig. S5) and contact angle measurements (Table S1) and finally using ellipsometry.



Scheme S2. Surface-confined synthesis of the photoiniferter monolayer on ITO surface.

The same synthetic procedure was also performed on smooth silicon wafer with native oxide layer. The sample was used for determination of the monolayer thickness using ellispometry.

Surface-initiated photoiniferter-mediated polymerization (SI-PMP) of MTEP monomer

The reaction system was composed of three glass vessels sealed with rubber septa and connected to each other with double tipped needles (commonly known as cannulas) in order to transfer the monomer under argon atmosphere. The reaction was performed in DMF/water mixture (not exceeding 9/1, v/v) with the monomer concentration 0.2-0.23 M (Table 1). The pure mixture of solvents was placed in the first vessel in order to saturate the reaction system by their vapors. The monomer solution was placed in the second vessel. The third vessel was made of glass which cuts off high energy radiation below ca. 290 nm. Inside this vessel a 2 mm thick quartz cuvette was placed that accommodated the ITO plate and a silicon wafer (behind the ITO plate) that reduced the optical path in front of the ITO sample to 200 μ m. Such reduction is necessary due to possible inner filter effect as MTEP absorption in UV region (see Fig. S4) partially overlays with the absorption of the photoiniferter.² The reaction system was purged with argon prior the transfer of the monomer solution to the third vessel with the ITO sample covered with the photoiniferter monolayer. Afterwards, the third vessel was placed in the photoreactor and irradiated for a given time under 300 nm irradiation (various number of lamps were used, see Table 1). After completion of the process the ITO plate with grafted polymer brushes was rinsed with copious amount of DMF, water, THF and additionally immersed in clean toluene and THF that were bubbled with argon and finally dried in the stream of argon.

Deprotectin of the acetylene groups in the multimonomer

After SI-PMP polymerization, the acetylene groups in the multimonomer chains were deprotected by treatment with potassium carbonate solution. The reaction was conducted in saturated solution of potassium carbonate in THF and methanol (1/1, v/v) at room temperature for 24h. After that the ITO plate was rinsed with copious amount of water, methanol, toluene and THF and then immersed in pure solvents solutions, bubbled with argon and finally dried in the stream of argon.

Quaternization polymerization of the acetylene groups

The deprotected acetylene groups in the multimonomer chains were polymerized by template polymerization. It was realized by treatment of the samples with ethyl iodide at 65°C for 72h. The sample with grafted multimonomers was placed in a glass vial with the mixture of 2 ml of ethyl iodide and 2ml of DMF. The glass vial was sealed with a rubber septum, purged with argon and heated in an oil bath to 65°C for a given time. Afterwards, the sample was removed from the vial, rinsed with copious amount of DMF, water, THF and then immersed in pure THF, bubbled with argon and finally dried in the stream of argon.

Synthesis of PNIPAM-3 brush

PNIPAM-3 brushes were synthesized using surface-initiated photoiniferter-mediated polymerization (SI-PMP) on the ITO surface. The reaction system was the same as for the polymerization of MTEP monomer. 5% aqueous solution of NIPAM monomer was used. The polymerization was conducted for 10 minutes under irradiation of 300 nm UV light (light power - 24 W). After completion, the ITO plate covered with PNIPAM brush was rinsed with copious amount of water and methanol and then dried in the flow of argon. The thickness of the brush was determined to be ca. 3 nm using AFM (scratch method).

Results

Spectroscopic characterization of the synthesized MTEP monomer



Figure S1. ¹H NMR spectrum of MTEP monomer.



Figure S2. ¹³C NMR spectrum of MTEP monomer.



Figure S3. IR spectrum of MTEP monomer.



Figure S4. UV-VIS spectrum of 0.1 mM solution of MTEP monomer in DMF.

Formation of the self-assembled monolayer of photoiniferter

The formation of the SAM on ITO was followed using grazing-angle reflectance IR spectra (see Fig. S5).



Figure S5. Grazing-angle reflectance IR spectra of the SAM of (chloromethyl)phenyltrimethoxysilane (A) and the same SAM after reaction with diethylammonium diethyldithiocarbamate (B).

The IR spectra after the first synthetic step (Fig. S5 A) showed the bands at: 1134 cm⁻¹ (s, v_s (Si-O)), 1450-1580 cm⁻¹ (m, v_s (C=C), aromatic), 2950 cm⁻¹ (w, v_s (C-H), alkane), above 3000 cm⁻¹ (w, v_s (C-H), aromatic). After the second synthetic step (Fig. S5 B) a few changes were observed: three bands appeared in the region between 1300-1400 cm⁻¹ (m, v_s (C-C) and v_{def} (C-H), alkane), 2880 and 2982 cm⁻¹ (w, v_s (C-H), alkane), 2825 cm⁻¹ (w, v_s (C-H) in CH₂-N group), 2675 cm⁻¹ (w, v_s (C-H) in CH₂-S group) These changes may be assigned to the presence of diethyldithiocarbamate (DTCA) groups attached to the monolayer after the second step. Therefore IR spectra confirmed that reaction proceeded properly. Moreover, the measured contact angle values (Table S1) are in a good agreement with the value for the grafted photoiniferter adsorbate (firstly synthesized in solution) monolayer obtained by G. Hadziioannou et.al. ³ on silicon surface.

Table S1. Contact angle measurements of the samples obtained during the synthesis of the SAM containing photoiniferter.

Sample	Contact angle [°]
Clean ITO surface	58 ± 3
After I step of synthesis	72 ± 2
After II step of synthesis	75 ± 2

The thickness of the photoinferter SAM deposited on silicon (ITO surface is too rough for such measurements) was determined to be ca. 0.9 ± 0.1 nm using spectroscopic ellipsometry. This value is smaller than the estimated length of the molecule (ca. 1.1 nm) indicating formation of a monolayer with substantial tilt of the molecules and/or partial disorder. This is consistent with presence of a bulky benzene ring and the lack of long aliphatic chains in the molecular structure that would promote denser packing of SAMs. The measured monolayer thickness should be taken into account in the measured overall thicknesses of the brushes (see further).

Thicknesses of PMTEP brushes

Thickness of the PMTEP brushes may be easily tuned by varying polymerization time and/or light intensity, monomer concentration. Dense PMTEP-22 brushes as thick as ca. 22 nm were obtained after 48h of polymerization with the other conditions similar to the ones reported in the main text (fig. S6).



Figure S6. Dry thickness measurements for PMTEP-22 brush (48h of polymerization) after SI-PMP.



Figure S7. Dry thickness measurements for: A) PNIPAM-3 brush after SI-PMP, B) PMTEP-3, C) PMTEP-5 and D) PMTEP-7 brushes after template polymerization.

UV-VIS characterization of PMTEP brush

The conjugated PMTEP-7 brushes were characterized by UV-VIS spectroscopy (Fig. S8). Due to the substrate (ITO) contribution to the measured spectra a differential spectrum was obtained. The spectrum for PMTEP-7 brushes after the first polymerization step was subtracted from the spectrum of the sample after the quaternization polymerization. The resulting spectrum exhibits rather broad band with maximum at about 570 nm that can be assigned to the conjugated chains in the brushes.



Figure S8. Differential UV-VIS spectrum in reflectance mode of PMTEP-7 brush after template polymerization.

Adhesion mapping of PMTEP brush

The adhesion of the PMTEP-7 was mapped using AFM (Fig. S9) at the border of the formed scratch. It is clear that the scanning AFM tip adheres much stronger to soft brush layer than to the bare ITO surface.



Figure S9. Adhesion image captured in PFT AFM mode for PMTEP-7 brush at the border with the bare ITO surface.

Current mapping of the doped PMTEP brush



Figure S10. AFM images of the doped PMTEP-7 brushes: (1.) tuna current mapping (25 mV DC sample bias) together with the respective current histogram, (2A.) topography, (3A.) adhesion, (4A.) peakforce error, and (2B.), (3B.), (4B.) the overlay plots of the current map with the respective topography, adhesion, and peakforce error images.

Figure S10 presents the overlaid images of the current map with topography, adhesion and peakforce error maps for doped PMTEP-7 brushes. The image 3B. shows some correlation between the high current spots and high adhesion (dark in the image) areas. There are practically no high current spots covering low adhesion (green) areas. There is clearly no correlation between current and topography (2B.) as high current spots occur on both low and high areas. Image 4B. may additionally support the conclusion on the lack of correlation between topography and current.

Swelling of PMTEP brush in water

PMTEP-7 brush was imaged using AFM in water and air and the topography images obtained in both media were compared (see. Fig. S11). The higher features observed in the image captured in water may be assigned to swollen chains that adapted more extended conformation due to repulsion interactions between the charged quaternized pyridines present in the brushes.



Figure S11. AFM topography images and the corresponding cross sections of PMTEP-7 brushes captured in water (A) and air (B).

Mechanism of the template polymerization in the brushes

Some additional experiments were prepared and performed to study the mechanism of the template polymerization. PMTEP brushes were deprotected and subjected to reaction with DMF solution of ethyl iodide at room temperature for 72 h in order to completely quaternize the pyridine rings. Afterwards, the temperature was increased to 65°C and the reaction was continued for 48 h. After this treatment the bands at about 3300 cm⁻¹ and 2098 cm⁻¹ were still visible in the FTIR spectrum (Fig. S12 B) indicating the presence of acetylene groups in the brushes. However, a shift of the -C-H bands (slightly below 3000 cm⁻¹) was observed confirming successful quaternization reaction. Furthermore, the appearance of the band at 1661 cm⁻¹, previously assigned to the stretching vibration of the quaternized pyridine ring, was observed. Subsequent treatment of the sample with fresh DMF solution of ethyl iodide at 65°C for 72 h gave virtually no surface reaction as the FTIR spectrum did not change (Fig.

S12 C). Thus, at room temperature quaternization of the pyridine rings proceeds preferentially while the polymerization of the acetylene groups is hindered. Moreover, if all the pyridine groups in the brushes are quaternized the polymerization does not proceed even at elevated temperature and in the presence of ethyl iodide. However, further treatment of the same sample with DMF solution of pyridine at 65°C led to the polymerization of the acetylene groups as indicated by the disappearance of the bands at 3300 cm⁻¹ and 2098 cm⁻¹ in the IR spectrum (Fig. S12 D). In addition, the band of carbonyl groups was shifted and a new band at 1608 cm⁻¹ was observed. It seems that the broad band observed for PMTEP brushes after regular template polymerization (Fig. 1C) is a consequence of overlapping of three bands 1735, 1661, 1608 cm⁻¹ presented in this case at different relative intensities (Fig. S12 D). After the treatment with pyridine the obtained conjugated chains may be rather short so the band observed previously at ca. 1620 cm⁻¹ might have been shifted to lower wavelengths (1608 cm⁻¹). Furthermore, the pyridine molecules from the solution were attached to the brush chains after nucleophilic attack that might also result in shifting of the band.



Wavenumber [cm⁻¹]

Figure S12. FTIR spectra of PMTEP brushes after the following steps: A) deprotection of the acetylene groups , B) reaction with ethyl iodide at 25° C for 72h and at 65° C for 48h, C) additional reaction with new portion of ethyl iodide at 65° C for 72 h, D) reaction with pyridine at 65° C for 72 h.

XPS measurements

XPS spectra were measured for PMTEP-7 brush after the first and the second polymerization steps. The bands for C1s were deconvoluated in order to determine contributions of different carbon atoms. In the spectrum after the first polymerization step, SI-PMP, (fig. S13 A) one may observe bands assigned to: C-Si slightly below 284 eV,^{4,5} C-(C,H) at about 285 eV, C-(O, N) at about 286 eV, C=O at 287 eV and O-C=O at 289 eV. After template polymerization the shape of C1s band changed significantly (fig. S13 B). C-Si band observed previously completely disappeared after deprotecion and subsequent template polymerization that is consistent with complete removal of protecting silane groups from the brushes. Moreover contribution from C-(O,N) increased indicating quaternization of nitrogen atoms by ethyl

iodide. Quternization reaction was also proven by the observed shift of the peak maximum for N1s from 399 eV before template polymerization (signal from nitrogen in pyridine) to about 400 eV after template polymerization (signal from nitrogen in quaternized pyridine) (see fig. S13 C).⁶ Furthermore, Si2p signal previously observed for the brush after SI-PMP (fig. S13 D) was not observed at all after template polymerization.

The experimentally determined contents of the mentioned types of carbon atoms are in good agreement with the theoretical calculations (see table S2) indicating that the first polymerization step as well as deprotection and quaternization reaction were successfully performed. Unfortunately, XPS measurements, in contrast to FTIR, cannot distinguish different hybridizations (sp, sp² and sp³) of carbon atoms that would be required for confirming formation of the conjugated chains in the second polymerization step (see discussion on FTIR spectra in the main text).



Figure S13. XPS spectra of: A) C1s for PMTEP brush after SI-PMP, B) C1s for PMTEP brush after template polymerization, C) N1s for PMTEP brush after SI-PMP and after template polymerization and C) Si2p for PMTEP brush after SI-PMP.

 Table S2. Contributions of various carbon atoms in PMTEP brushes as determined using XPS.

	After SI-PMP		After template polymerization	
	Theoretical	Experimental	Theoretical	Experimental
Type of carbon	Contribution [%]	Peak area [%]	Contribution [%]	Peak area [%]
<u>C</u> -Si	28.6	35.5	0	0
<u>C</u> -(C,H)	50.0	45.8	69.2	72.0
<u>C</u> -(O,N)				
<u>C</u> =O	21.4	18.7	30.8	28.0
O- <u>C</u> =O				

Estimation of the conductivity of the doped PMTEP brushes

Electrical conductivity (σ) values for the doped PMTEP brushes were calculated using a simple formula (eq. 1)

$$\sigma = 1/RS \tag{1}$$

where:

S - the tip-surface contact area;

l - the average length of the brush chains;

R - the electrical resistance of the brushes that was taken as an average reciprocal slope of the curves in the linear part of the I–U plots (see Fig. S14) in the voltage range between -0.1 V and +0.1 V (low voltage ohmic region).



Figure S14. Representative the I-U plots for: A. – nonconductive sample, B. – conductive polymer and C. – conductive ITO.

Assuming small indentation of the tip (nominal tip radius 25 nm, external load close to zero) into the brush the contact area (S) may be estimated on the level not larger than 10^{-17} m². The actual dry thickness of the brush was taken as a chain length (3-7 $\cdot 10^{-9}$ m). The electrical resistance (R) for PMTEP-3 may be estimated to be 10^{8} - 10^{9} Ω based on the histogram (Fig. 4C, dI/dU $\approx 10^{3}$ - 10^{4} pA/V). It results in the conductivity values on the level 10^{-1} - 10^{0} S/m. Similar estimations for the thicker brushes (see Fig. 4 D and E, dI/dU $\approx 10^{1}$ - 10^{4} pA/V) lead to conductivity values 10^{-3} - 10^{0} S/m.

References

- 1 T. Sasaki, J. M. Guerrero and J. M. Tour, Tetrahedron, 2008, 64, 8522-8529.
- 2 E. M. Benetti, S. Zapotoczny and G. J. Vancso, Adv. Mater., 2007, 19, 268.
- 3 B. de Boer, H. K. Simon, M. P. L. Werts, E. W. van der Vegte and G. Hadziioannou, *Macromolecules*, 2000, **33**, 349-356.
- 4 S. Ciampi, T. Bo[°]cking, K. A. Kilian, M. James, J. B. Harper and J. J. Gooding, *Langmuir* 2007, 23, 9320-9329.
- 5 E. J. Nemanick, P. T. Hurley, L. J. Webb, D. W. Knapp, D. J. Michalak, B. S. Brunschwig and N. S. Lewis, *J. Phys. Chem. B* 2006, **110**, 14770-14778.
- 6 K. Jurewicz, K. Babeł, R. Pietrzak, S. Delpeux and H. Wachowska, Carbon 2006, 44, 2368–2375.