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ARTICLE

Conductive Polythiophene-based Brushes Grafted from ITO Surface via Self-Templating Approach

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Conductive polythiophene-based brushes grafted from indium tin oxide substrate were fabricated as promising materials with directional conductivity feature for potential optoelectronic applications. The obtained brushes, thanks to their ordered structure and large conjugation length, exhibited high conductivity after chemical doping. Surface-initiated photoiniferter mediated polymerization of 3-methylthienyl methacrylate monomer was used in the first step of grafting enabling formation of dense brushes. In the second step self-templating approach that utilized oxidative polymerization of the pendant thiophene groups in the grafted multimonomer chains was used for the formation of ladder-like conjugated brushes. The polymerization conditions were optimized towards the largest possible effective conjugation lengths of the macromolecules. The rate of the undesirable spontaneous iodine dedoping process was followed for the first time using conductive Atomic Force Microscopy. UV-VIS and grazing angle IR spectroscopy were applied to find correlations between various synthetic procedures and the conjugation lengths of the brushes.

1. Introduction

Conjugated polymers have gained great interest because of their unique electrical and photophysical properties attractive for numerous applications.[1] These types of polymers are in their native form semiconductors but after chemical modifications they exhibit conductivity nearly on the same level as metals. Due to low cost of production, flexibility, variety of chemical structures and materials morphologies, conjugated polymer-based optoelectronic devices appear to be a serious alternative for commercial inorganic ones. Polythiopene-based polymers are especially very promising because of high environmental stability, broad absorption spectra reaching long wavelengths and high charge mobility. Therefore, such polymers found applications in: organic light emitting diodes,[2] field-effect transistors,[3] organic photovoltaics,[4,5,6] flexible electronics,[7] supramolecular organic semiconductors[8] or in biomedical field[9] such as superhydrophobic biointerface[10] and scaffolds.[11]

Conductivity of materials based on conjugated polymers is determined by two main factors: interchain and intrachain charge transport.[12] The interchain conductivity path is mainly determined by carriers hoping frequencies between neighbouring polymer segments while mean effective conjugation length influence intrachain charge transport.[12] Thus, in order to obtain well-conducting system conjugation length and macromolecular arrangement have to be both optimized. Conjugation length in polythiophenes (PTs) may be easily followed by UV-VIS and IR spectroscopy. With the increasing conjugation length the wavelength of π-π* electron absorption maximum also increases.[13] Conductivity of the PTs strongly depends on type of dopant. PTs doped with iodine may exhibit conductivity as high as 1000 S/cm[14], however as presented by Koizumi et. al.[15] iodine undergoes fast sublimation from the sample and conductivity after about 1h dramatically decreases by a few orders of magnitude. Moreover, after repeated doping the measured conductivity is much lower when compared to the initial doping.

Conjugated polymers are usually synthesized in solution. However, most of their applications require formation of polymeric layers on surfaces. Unfortunately, polymeric cast films deposited on surfaces are susceptible to degradation by physical processes of abrasion, delamination or thermal expansion.[16] Furthermore, conductivity of conjugated polymers in cast films is hindered due to the disturbed transport of charge carriers as macromolecules in bulk are disordered. Thus, there is a strong demand on formation of ordered or self-assembled polymer systems[17] that may easily processed and exhibit high stability and conductivity. Surface grafting is one of the methods, which enable formation of

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Electronic Supplementary Information (ESI) available: additional results of AFM measurements, grazing angle IR spectra, estimations of the brush conductivity and a movie showing C-AFM images changing in time. See DOI: 10.1039/x0xx00000x stable platform of covalently attached conjugated macromolecules that are perpendicularly oriented to the surface.[18] Such orientation allows directional transport of charge carriers along the stretched conjugated macromolecules as it is desired in order to facilitate charge injection and extraction.[19]

Conjugated surface-grafted polymer brushes are an example of such materials. These polymeric layers can be synthesized via “grafting form” or “grafting to”[20] approaches. However, only the “grafting from” process enables formation of well-ordered, dense brushes. Nonconjugated polymer brushes are commonly synthesized using surface-initiated controlled radical polymerizations (SI-CRP),[21,22] because such methods enable control over brush thickness, architecture, end-functionality and final material morphology.[23,24] However, formation of conjugated polymer brushes cannot be directly realized by such powerful and versatile methods like SI-CRP. Step growth mechanism of polymerization or polycondensation dominates for the synthesis of conjugated polymers. In this techniques combination of “grafting from” and “grafting to” approaches are used (often call as “grafting through”) because polymerization starts simultaneously both in solution and at the surface. An example of such technique is chemical oxidative polycondensation with e.g. $FeCl_3$ as an oxidizing agent. This technique was used by Le et al.[25] for the formation of carbon nanotubes decorated with poly(3-hexylthiophene) (P3HT) brushes. Such oxidative polymerization appears to be an undemanding method that is easy to perform. However, problems with control of brush thickness and grafting densities, remaining impurities and higher surface roughness significantly reduce applicability of such techniques in e.g. optoelectronics devices. The mentioned problems are limited in some metal catalyzed polycondensations[26,27,28,29,30] due to chain growth mechanism which is compatible with “grafting from” approach. Nevertheless, such polymerizations often require restrictive conditions such as: very pure reagents, low temperatures and specially modified monomers. Polymerization of large monomers is hindered due to complex catalysis process with "walking" nickel-based catalyst[18] like in the most popular surface-initiated Kumada catalyst transfer polycondesation. Formation of copolymer brushes seems to be also very limited as these techniques are rather designed for the formation of homopolymer polythiophene or polypryrrole based brushes.

Very recently, we have presented a novel synthetic approach, which utilized self-templating surface-initiated polymerization (ST-SIP) for the formation of ladder-like conjugated polyacetylene brushes.[31,32] Such approach enables formation of complementary conjugated macromolecules with similar polymer chain length as the template macromolecule. In the first step methacryloyl groups in the used bifunctional monomers[31,32] were polymerized using surface-initiated photoiniferter-mediated polymerization (SI-PMP) which is one of SI-CRP method. This photopolymerization was introduced in solution by Otsu et al.[33] and later on was also successfully applied for the formation of surface-grafted brushes offering facile control on the kinetics,[34] chain ends of the macromolecules,[35] and formation of block copolymer brushes.[36,37,38] In the second step of ST-SIP, template polymerizations were conducted for the pendant acetylene groups of the formed multimonomer brushes. The obtained conjugated brushes after doping exhibited high conductivity with ohmic characteristics. Thus, similarly attractive features may be expected for other conjugated brushes fabricated via ST-SIP especially the ones based on polythiophene that is a commonly used backbone in various optoelectronic applications.

In the current work we present formation of poly(3-methylthienyl methacrylate) brushes (PMTM) with their thickness ranging from a few to more than 200 nm obtained in self-templating polymerization approach. MTM monomer was polymerized by SI-PMP in the first step and subsequently the pendant thiophene groups were reacted using simple oxidative polymerization with $FeCl_3$ as an oxidizing agent. Such polythiophene-based materials have desired optoelectrical properties for photovoltaic and electronic applications. The obtained brushes had active ends as they easily undergo chain extension process so the thicknesses of the brushes may be easily tune by changing light intensity, monomer concentration or polymerization time. The presented here approach is very versatile and easy to perform at undemanding conditions. The resulted brushes after doping exhibited very high conductivity 1-2 orders of magnitude higher than for the same polymers obtained in solution.

2. Experimental

2.1 Reagents and materials

Thiophene-3-methanol (98%), magnesium sulfate (anhydrous 99.5%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Triethylamine (TEA>99%), methacryloyl chloride (≥97%, distilled before usage), diethylthiocarbamic acid diethylammonium salt (97%), iodine (≥99.8%), copper(I) chloride (anhydrous, beads, ≥99.99% trace metals basis) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Dichloromethane (p.a), diethyl ether (p.a.), toluene (p.a.), dimethylformamide (p.a.), chloroform (p.a.) were all purchased from Chempur (Piekary Slaskie, Poland). (*p*-chloromethyl) phenyltrimetoxysilane (95%) was purchased from ABCR (Karlsruhe, Germany). Ammonia solution (25% p.a.), hydrochloric acid (35-38% p.a.), sodium hydroxide (p.a.) were obtained from POCH S. A. (Gliwice, Poland). Hydrogen peroxide (30% p.a.) was purchased from Stanlab (Lublin, Poland). Tetrahydrofuran (p.a), acetonitrile (for liquid chromatography), nitromethane (for synthesis) were obtained from Merck (Whitehouse Station, NJ, USA). Iron(III) chloride (99.5%) was obtained from Lab-Scan (Gliwice, Poland).

2.2 Methods

FTIR spectra of PMTM brushes on ITO surface were recorded using Nicolet iS10 FT-IR spectrometer with grazing- angle reflectance accessory (84° angle was used for all the measurements). The UV-VIS spectra of the brushes were measured on Varian Cary 50 UV-VIS spectrometer. 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). C-AFM (conductive AFM) mode was used for conductivity imaging (bias voltage 3000 mV) and collecting of I/U curves (see further). PeakForce TUNA mode (tunneling AFM) was used for collecting of I/U curves for lower voltages range (-500 mV to 500 mV). 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 using ramp mode with low setpoint value and the voltage applied between the tip and the sample surface that was ramped in the range -500 mV to 500 mV in one case and -5000 mV to 5000 mV in another case (see further). The plots were recorded for a given time after doping at least in 16 positions on a surface.

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

The self-assembled monolayer (SAM) containing photoiniferter head groups on ITO surface was fabricated as previously reported by our team.[31] The obtained MTM monomer was polymerized using SI-PMP by exposure the samples to UV light using broadband Xenon lamp light source (Laser Driven Light Source, ENERGETIQ LDLS^{TM}) with light intensity about 3000 mW/cm^2 as measured for 312 nm using radiometer VLX 3W. The reaction system with three vessels sealed with rubber septa was used. All the vessels were connected by cannulas and the whole system was purged with argon. The first vessel contained pure DMF in order to saturate the flowing argon with the solvent vapours. Solution of the obtained MTM monomer in DMF with concentration 0.66 M was placed in the second vessel. The quartz cuvette with modified ITO plate was placed into the third vessel made of glass that cuts off high energy radiation below ca. 290 nm. The monomer solution was transported from the second to the third vessel by needle under argon pressure and the third vessel was exposed to the UV irradiation. After completion of the polymerization the sample was cleaned by extensive rinsing with DMF, CH_2Cl_2, THF, toluene and finally dried in the stream of argon. PMTM brushes of different thicknesses were obtained by varying the polymerization conditions: time, monomer concentration, and/or light intensity.

2.3 Oxidative polymerization of PMTM brushes with $FeCl_3$

The conditions of oxidative polymerizations were optimized by varying e.g.: solvent, temperature and initial catalyst concentration. Solutions of $FeCl_3$ (0.13 M) in various solvents (freshly distilled $CHCl_3$, additionally dried $CHCl_3$, CH_3CN, CH_3NO_2) were used. The ITO surface with the obtained PMTM brushes was dipped in a given solution for 20 hours in argon atmosphere and in an ice bath if required to keep the temperature low. After completion of the polymerization, the sample was cleaned by rinsing with copious amounts of CH_2Cl_2, THF, HCl (0,1 M), H_2O, THF (again), toluene and finally dried in the stream of argon. In order to test, how slow addition of catalyst influence the process, solution of the $FeCl_3$ in CH_3NO_2 (0.13 M) was added dropwise during 2 hours from the purged vessel to the vessel containing the substrate immersed in 5 ml of CH_3NO_2 at 0°C. Afterwards, the sample was left in the ice bath for next 4 hours and moved to room temperature for next 14 hours. The cleaning of the substrate was the same as mentioned above.

2.4 Doping of PMTM brushes with I_2

The ITO plate with grafted PMTM brushes after oxidative polymerization was placed in a sealed vessel with saturated vapours of I_2 for one hour.

3. Results and discussion

3.1 Surface-initiated photoiniferter mediated polymerization (SI-PMP)

Bifunctional MTM monomer with methacryloyl and thiophene groups in its structure was synthesized following the procedure previously reported by Çirpan et al.[39] and used for the formation of conjugated polythiophene brushes. In the first step monolayer of the photoiniferter containing initiator was formed on ITO surface. After that methacryloyl group in MTM monomer was polymerized using SI-PMP from conductive ITO surface forming grafted multimonomers with thiophene pendant groups (scheme 1 A and B).

The choice of ITO substrate was determined by excellent stability of the brushes formed on its surface and broad applicability of such materials in optoelectronic devices. Different brush thicknesses were obtained by varying the reaction time, monomer concentration and applied light intensity. For conductivity studies four samples were chosen with the dry thicknesses of 6 (PMTM6), 12 (PMTM12), 45 (PMTM45) and 215 nm (PMTM215) mainly obtained by varying the time of SI-PMP (see table 1 and fig. S1 A). The formation of polymer brushes after SI-PMP process was followed by FTIR

Scheme 1. Synthetic route to ladder-like conductive PMTM brushes.

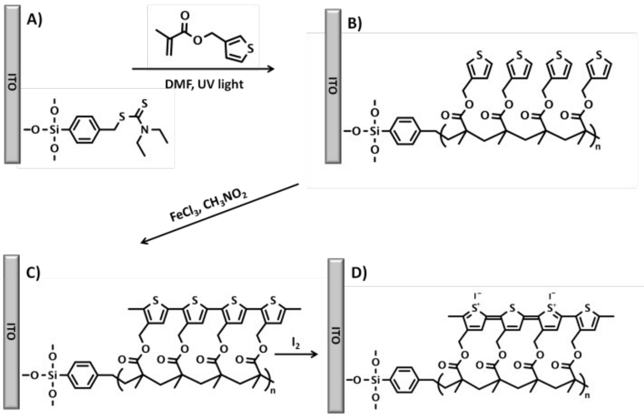

Table 1. Conditions of SI-PMP process with measured dry brush thicknesses after SI-PMP, template polymerization (with $FeCl_3$) and iodine doping.

Name	Time of SI-PMP [h]	Monomer concentration [w/w %]	Power of light [mW/cm^2]^1	Thickness after SI-PMP [nm]	Thickness after template polymerization [nm]	Thickness after iodine doping [nm]
PMTM6	1	12.4	3000	6	10	13
PMTM12	2+2	12.4	2500	(6) 12	15	20
PMTM45	4	12.4	3000	45	55	90
PMTM215	20	12.4	3000	215	260	290

^{1} Measured for 312 nm light wavelength.

grazing angle spectroscopy (see fig. 1) and AFM. The IR spectra of the obtained PMTM brushes contained the same bands as in the spectrum of this polymer obtained in solution.[40] The observed characteristic bands of thiophene ring (3105 cm^{-1} for α-CH stretching vibration, 1480 cm^{-1} for C=C symetric stretching vibrations, 790 and 694 cm^{-1} for α-CH and β-CH out of plane bending)[41] and methacryloyl group (2998, 2955, 2888 cm^{-1} for CH stretching vibrations in alkyl group, 1731 cm^{-1} for C=O stretching vibration in ester group) confirm the formation of PMTM brushes. The AFM topography measurements indicated uniform coverage of the ITO by PMTM brushes (see fig. S1 B). The average roughness value (R_a) measured for PMTM215 after SI-PMP was on the level of 0.92 nm, which is very low confirming formation of uniform smooth polymer layer.

Due to the fact that SI-PMP is a controlled radical polymerization the obtained brushes should have active chain-ends and the polymerization may be reinitiated on demand. In order to verify this the PMTM brush with the thickness of 6 nm obtained after 2h of SI-PMP (see fig. S2 A) was again polymerized for the next 2h and the thickness increased up to 12 nm (fig. S2 B). This chain extension experiment indicates that the formation of copolymers with different monomeric units is possible in this procedure while it is hardly possible for e.g. Kumada, Stile or Suzuki polycondensations that were used so far for preparation of polythiophene based brushes.

3.2 Template oxidative polymerization with $FeCl_3$

After Si-PMP thiophene pendant groups in the obtained grafted multimonomer chains (scheme 1B) were polymerized using oxidative polymerization with $FeCl_3$. After this step intensity of the previously observed band at about 3105 cm^{-1} was significantly decreased. Moreover, the band at about 790 cm^{-1} (α-CH out of plane bending in thiophene ring) was shifted to longer wavelengths (see fig. 1B). New bands at about 1520-1560 cm^{-1} and 1656-1680 cm^{-1} (C=C asymmetric stretching vibrations in polythiophene chain) appeared (fig. 1B). All this changes fully confirm formation of conjugated polythiophene chains and are very well described in the literature for different polythiophene-based polymers.[41,42,43] Furthermore, brush thicknesses increased for all the studied samples (see table 1 and fig. S1 A and C) as well as the average roughness value R_a (fig. S1 B and D). Such effects may be explained by stiffening of the brushes after formation of the conjugated chains implying that they get extended in their dry state (larger thickness) and do not fill the gaps among them (higher roughness) that are formed due to certain distribution of their lengths.

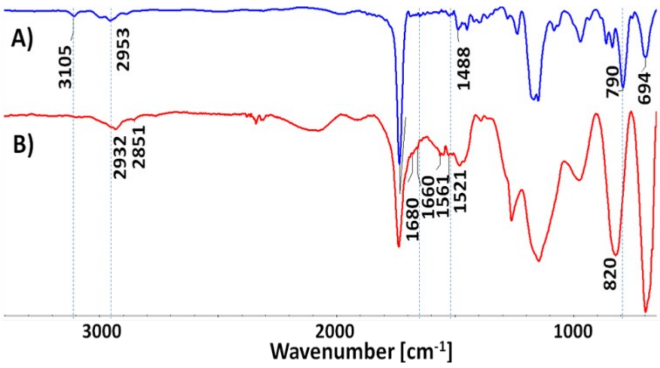

Fig. 1 FTIR spectra of PMTM12 brushes: A) before and B) after template polymerization.

3.3 Influence of oxidative polymerization conditions on brush conjugation length.

Different conditions of oxidative polymerization were tested in order to optimize the conditions that enable formation of brushes with large effective conjugation length. At the beginning for two PMTM brushes of similar thickness (70-80 nm) chloroform was used as the most common solvent for the applied oxidative polymerization. Polymerizations were conducted at room temperature under argon atmosphere. In one case freshly distilled chloroform was used while in another one the solvent was additionally dried under molecular sieves. As it is clearly visible in the UV-Vis spectra (fig. 2B) the obtained conjugation length for the brushes are rather small, because absorption maximum in one case is c.a. 350 nm while for extra dried chloroform it is 360 nm. It corresponds to the conjugation length of only 3 thiophene units according to data presented by Izumi et. al.[13] However, for the dried chloroform some broadening of UV-VIS band was observed which may be assigned to formation of macromolecules with larger conjugation length. In the next step, dried chloroform was used and the reaction was conducted for 6h at 0°C and than for 14h at 25°C. For the brushes as high as 170 nm, a new small band at about 430 nm appeared (fig. 2A). However, the ratio between the observed band at 430 nm to huge band at about 350 nm is rather small. It means that longer effective conjugations were obtained but only for small part of the chains. Moreover, the obtained IR spectra (fig. S3 C) showed

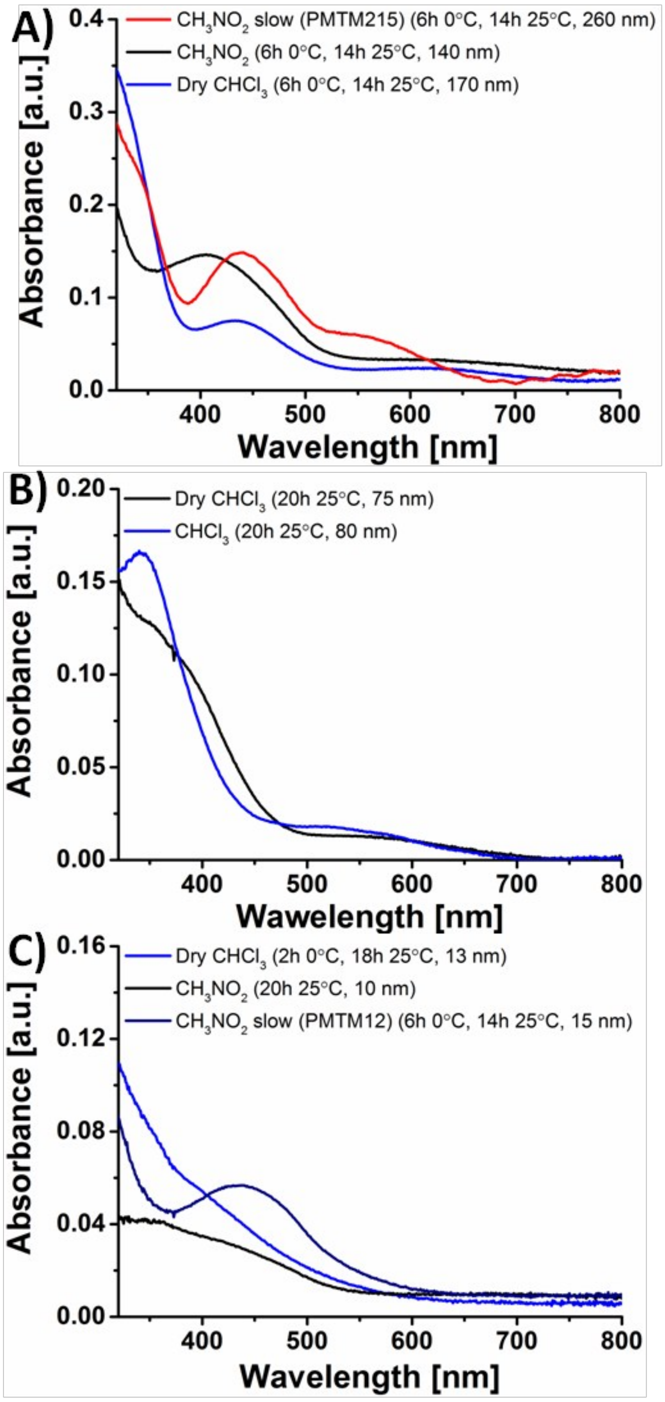

Fig. 2 UV-VIS spectra of PMTM brushes polymerized in different conditions during template polymerization: A) with large thickness (140-260 nm), B) with medium thickness (75-80 nm) and C) with small thickness (10-15 nm).

that the conjugation is rather low because of very high ratio of intensities of I_{1520}/I_{1480} and I_{1660}/I_{1480} as described elsewhere.[41,43,44] Thus, one may conclude that cooling down the reaction mixture at the beginning of the process increases the content of chains with longer effective conjugation. However, chloroform was also found as not particularly good solvent for polymerization of thiophene rings in PMTM brushes. The most likely explanation of this phenomenon is a limited solubility of $FeCl_3$ (oxidizing agent) in chloroform leading to heterogeneous conditions of the polymerization in this solvent that also limits diffusion of the oxidizing agent to the lower parts of the brushes. Longer conjugations were obtained when nitromethane was used as a solvent. It is expected that due to very good solubility of $FeCl_3$ in this solvent, the Fe^{3+} ions may easily reach bottom of the brushes and effectively promote the polymerization. The measured UV-VIS spectra were significantly red shifted when compare to the spectra obtained for polymerizations conducted in chloroform (fig. 2). Moreover, it was found that by reducing the temperature during oxidative polymerization the obtained conjugation lengths were even larger as the UV-VIS absorption maximum was red shifted (see fig. 2C). Furthermore, slow addition of the catalyst led to further elongation of the conjugation (see fig. 2A) that is in a good agreement with similar experiments described elsewhere for PT based polymers obtained in solutions.[45,46] For the thinner brushes the same trend was observed (see fig. 2C and fig. S4).

Therefore, the best conditions were found for the polymerization conducted in nitromethane at low temperature and with slow addition of the oxidizing agent. However, it appeared that the average conjugation length and distribution of the chains with various conjugation lengths in the brushes depend largely on the brush thicknesses. PMTM brushes with different thicknesses were obtained using SI-PMP and than polymerized by template polymerization at the same optimized conditions (see table 1). It was observed within the studied thickness range (10-260 nm) that the thinner the brush the higher the obtained conjugation length (see fig. 3 and fig. 4). UV-VIS spectra (fig. 3) showed that when the brush thickness increases the ratio of the absorbance at about 450 nm and 320 nm decreases. It means that the content of the polymer chains with higher conjugation length decreases with increasing brush thickness.

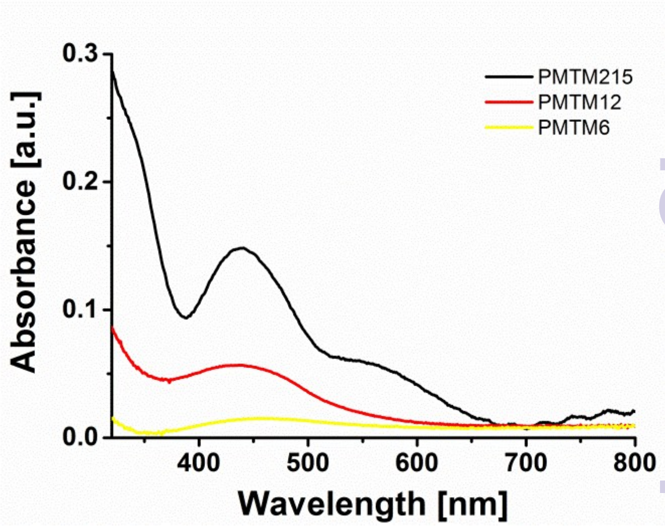

Fig. 3 UV-VIS spectra of PMTM brushes with different thicknesses after template polymerization ($FeCl_3$ as oxidising agent) in CH_3NO_2 (with slow addition of $FeCl_3$) at 0°C for 6h and than at 25°C for 14h.

The observed relationship was also confirmed by the measured IR spectra for which ratios of intensities of the following IR bands I_{1520}/I_{1480} and I_{1660}/I_{1480} were compared. The largest intensities of the bands at about 1520 and 1660 cm^{-1} were observed for thin brushes (10 and 15 nm) while for thicker brushes those intensities were smaller. Moreover, when IR spectrum of the brush as thick as 260 nm polymerized at the optimized conditions (fig. S2 A) was compared to the IR spectra of the thinner brushes obtained in nitromethane (140 nm) and dry chloroform (170 nm) (fig. S3 B and C) at low temperature no significant differences were observed. It was found that the average conjugation length was the largest for the 140 nm brush obtained using polymerization in nitromethane (see fig. S3) although the most red-shifted absorption maximum was found for 260 nm brushes obtained at the optimized conditions (fig. 2A). It means that UV-VIS spectra may be used to follow distribution of the polymer chains with various conjugation lengths. Thus, the fraction of chains with the highest conjugation length was observed for 260 nm brushes although only in small content so the average conjugation length observed by IR remained low. Therefore, the longest average conjugation lengths were obtained for the thin brushes with the thicknesses after template polymerization respectively: 10 and 15 nm (PMTM6 and PMTM12). It is important to mention that very recently Saha et al. have successfully polymerized MTM monomer from ITO surface using surface-initiated Atom Transfer Radical Polymerization.[47] Unfortunately, pendant thiophene rings in the formed PMTM brushes could not be polymerized by the proposed electrochemical approach due to low reactivity as it was noticed by the authors. Moreover, even electrochemically polymerized brushes with tertthiophene pendant group exhibited small conjugation length (absorption maxima at. 370 nm). The authors noticed, that the main products of such polymerizations are hexamers. Thus, it seems that the presented here optimized conditions of chemical oxidative polymerization is more suitable method when compare to the proposed by Saha et al. PMTM brushes obtained in this report posses higher conjugation lengths because the obtained UV-VIS maxima are significantly red shifted and lay at about 440-450 nm.

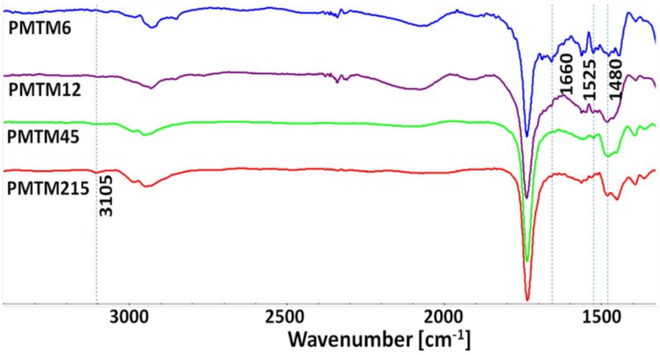

Fig. 4 IR spectra of PMTM brushes with different thicknesses after template polymerization ($FeCl_3$ as oxidising agent) in CH_3NO_2 (with slow addition of $FeCl_3$) at 0°C for 6h and than at 25°C for 14h.

3.4 Conductivity measurements

The iodine doped PMTM brushes exhibited high conductivity when measured by collecting current vs voltage plots. The measured conductivity values for brushes with different thicknesses were found to reach the level of 10^{-2} S/cm (see table 2). I/U plots captured for all the samples exhibited linear ohmic character (see fig. S5). It is very important to emphasize that the conductivities were measured after the second iodine doping which may significantly lowered the obtained values as described elsewhere.[48] In order to verify this observation another sample was freshly doped and its conductivity was measured after the first doping at the same conditions. For the brush with the thickness of 90 nm (PMTM45) the measured dI/dU value was 2.35 nA/V that corresponds to the conductivity value on the level of 0.2 S/cm (see SI for the details of the estimation method).

3.5 Iodine dedoping

It was found that conductivity of the obtained brushes decreases in time after iodine doping which is in a good agreement with the previously obtained results.[48,49] It can be clearly seen even during capturing of a single C-AFM image (see fig. 5). Possible contribution of contamination of the AFM tip can be excluded here since the consecutive measurements for the used tip and freshly doped samples led to similar results as presented in fig. 5. Moreover, C-AFM images captured in 2 minutes intervals (see ESI) indicated that the largest decrease in conductivity occurs immediately after iodine doping. In order to quantify these changes for PMTM45 after second doping the respective plots were captured for a prolonged time (fig. 6). For each datapoint at least 16 I/U plots were capture by ramping from -500 mV to 500 mV and the average slopes captured for the plots are presented in the graph (fig. 6). It was found that the conductivity of the brush dramatically decreases with time (7 times during 40 minutes). However, the observed linear decrease is even weaker than previously reported for similar polymers in bulk although faster decrease cannot be excluded in the first 20 min (due to technical limitation the C-AFM measurements could not be performed earlier than 20 min after doping). Even the obtained brushes seem to be dedoped slower than classical films for applicability of those structures other than iodine doping agents should be applied (work in progress).

Table 2. Conductivity measurements in C-AFM mode after second doping in iodine vapours.

Sample	Time after iodine doping [min]	dI/dU[a] [nA/V]	Estimated conductivity [S/cm]
PMTM6	40	2.10±0.03	0.03
PMTM12	20	2.88±0.04	0.06
PMTM215	40	0.043±0.001	0.01

[a] I/U plots were ramped in the range from -5000 to 5000 mV

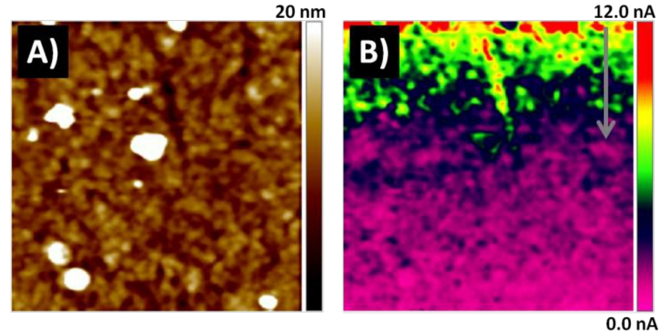

Fig. 5 A) AFM topography image (5x5 µm) of freshly doped PMTM12 (second time) with B) corresponding C-AFM mapping with the arrow indicating the direction of frame capturing (8 minutes per frame).

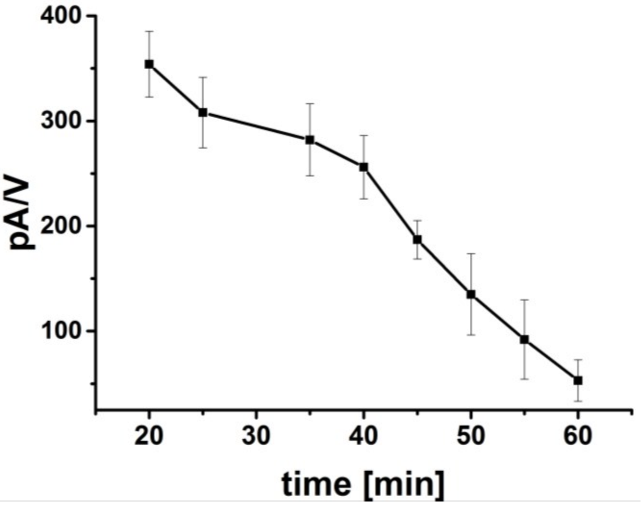

Fig. 6 The graph showing relationship between slopes of captured I/U plots at given time and time after iodine doping.

4. Conclusions

We proposed here a facile strategy for the synthesis of ladder-like polythiophene-based conductive brushes. The method enabled formation of well-ordered brushes with thicknesses ranging from 6 to 215 nm. It was shown that the obtained brushes have active ends as it was indicated in the chain extension experiment. Thus, it enables easy formation of block copolymer brushes including combinations of segments with various conductivity. The developed here self-templating oxidative polymerization with $FeCl_3$ may serve as a simple method for the formation of platforms of perpendicularly oriented conductive macromolecules.

We tested a number of different polymerization conditions in order to form PMTM brushes with the longest effective conjugation length that directly influence the conductivity. Nitromethane was recognized as the optimal solvent for that process. Furthermore, slow addition of $FeCl_3$ and cooling of the reaction system enhanced the conjugation lengths observed in the brushes. It was also found that the brush thickness had a profound impact on the final conjugation lengths. The brushes obtained here had significantly longer conjugation lengths in comparison to similar brushes obtained by electrochemical approach.[47]

Conductivity measurements by C-AFM revealed high conductivity of the doped brushes in the direction perpendicular to the surface ranging from 10^{-1}-10^{-2} S/cm. Such values are 1-2 orders of magnitude higher than the ones measured for the same polymers obtained in solution during electrochemical polymerization.[39] Dedoping rate of iodine-doped PMTM was followed by C-AFM conductivity mapping for the first time. It was found that conductivity decreases so fast that significant changes may be observed even within a single AFM image. This process was also quantified by measuring I/U plots over prolonged time. It was revealed that conductivity of iodine-doped PMTM brushes decreases approximately linearly with time within the studied range.

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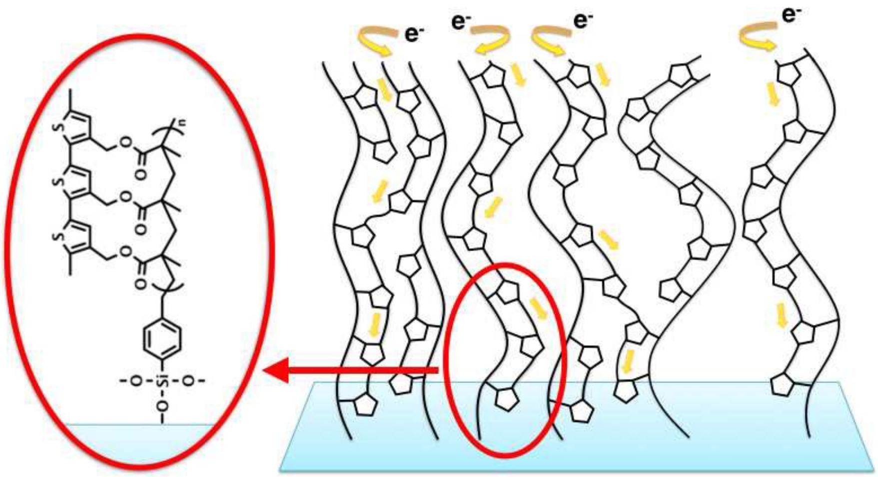
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