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One Step Lithography of Polypyrrole**

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Large areas of polypyrrole (PPy) thin films deposited onto inert polymeric substrates are structured by direct laser interference patterning (DLIP). Several square millimeter areas could be produced with one single (10 ns) pulse, at room temperature and atmospheric pressure. Nanometric arrays of lines (>600 nm) or grids of PPy deposited on dielectric polymers polypropylene or polypyrrol (PP or PE) are fabricated by DLIP at 355 nm. The period of the lines structures, measured by white light interferometry (WLI), is 3.5 μm . Regular structures are analyzed using scanning electron microscope (SEM) and a focus ion beam (FIB) tomography. It is shown that only the PPy film is structured while the PP or PE substrate remains unaltered. Fourier transform infrared spectroscopy (FTIR) and UV-vis spectroscopy, permit to ensure that PPy chemical structure remains unaltered after the structuration process. The width of PPy lines can be tailored by controlling the fluence of the laser beam. Contact angle measurement shows that the wettability is affected by the structuring, making the surface more hydrophobic. The structuring technique seems to be suitable for the fabrication of PPy regular structures over various substrates.

Materials containing π -conjugated polymers present very interesting properties, and their application in electronic and optoelectronic devices (such as solar cells, light emitting

diodes, electronic memories, etc.) is being explored intensively.^[1] Among them, polypyrrole (PPy) can be reversibly modulated by doping or dedoping different ions,^[2] offering it many potential applications in various devices such as microactuators, and microfluidic devices.^[3–5] PPy can be also used in biological applications such as neural electrodes,^[6,7] and scaffolds for nerve regeneration in neural-tissue engineering,^[8–10] because it retains its conductivity in neutral media. A key factor in those applications is the control of polymer surface roughness. To increase PPy surface roughness, different techniques has been explored, such as the creation of porous films using polystyrene sphere templates,^[11] the fabrication of composites of nanoparticles and polylactide^[12] the growth of conducting polymers within hydrogels,^[13] and the blend with biomolecules to yield “fuzzy” structures.^[14] Another way to achieve control of surface roughness involve micro/nanometric structuring of the surface. Conventional photolithography is difficult to use because involve aggressive chemistry and thus can degrade the backbone. Non-photolithographic approaches avoid those degrading factors. Therefore, inkjet lithography,^[15] soft lithography,^[16] and hot-embossing lithography,^[17] have been used to structure PPy. However, they have low throughput in generating patterning or they employed masters that may have undesirable deformations, such as pairing, sagging, and shrinkage. Gomez *et al.*, reported the fabrication of 1 and 2 μm wide microchannels in PPy using electron-beam (e-beam) lithography and electropolymerization, employing a various step to obtain the desired patterning.^[6]

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In the present communication we describe a method to structure PPy in a simple manner using direct laser interference patterning (DLIP). The technique can be used to fabricate micro/nanometric structures of polymer surfaces in a single step, producing a very regular patterning, with the possibility to obtain diverse regular structures (line, dots, nets) on large areas (up to cm^2).^[18,19] Moreover, no additional process steps (i.e., etching, development of photoresist, and mask fabrication) are required. We have shown that polyaniline (PANI) layers, deposited onto polycarbonate or polyimide, can be structured by DLIP.^[20] The PANI conductive polymer arrays generated in this manner could be used as sensors.^[21] However, PANI arrays are not useful in biological environment because PANI is not conductive in neutral media.

Here, it is shown that DLIP can produce regular arrays of PPy lines or grids in one step. The topography of the arrays is studied using white light interferometer (WLI) and scanning electron microscope (SEM). The physicochemical properties of the structured PPy are evaluated by FTIR, UV-vis spectroscopies and conductivity measurements. The wettability of the surface, an interesting property for biological applications, is evaluated by measuring the contact angle of water.

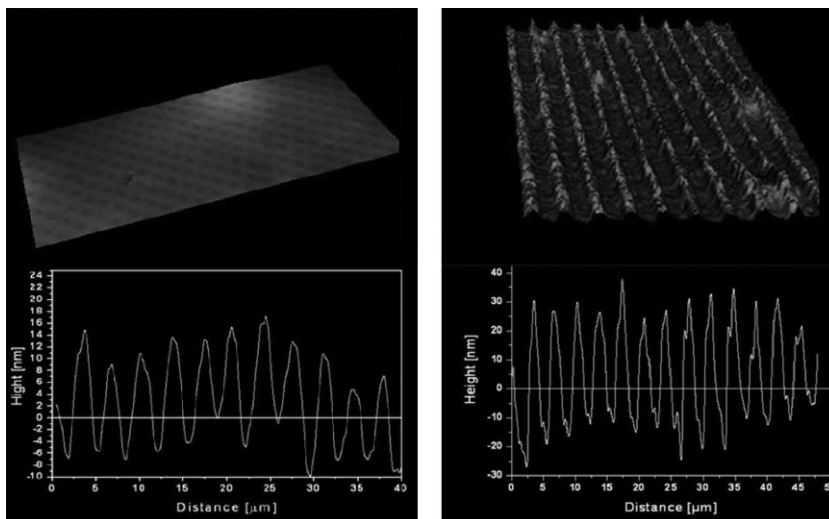


Fig. 1. WLI images of PPy nanometric structures supported onto PP (a) lines, laser fluence = 220 mJ cm^{-2} ; (b) grid, laser fluence = 58 mJ cm^{-2} .

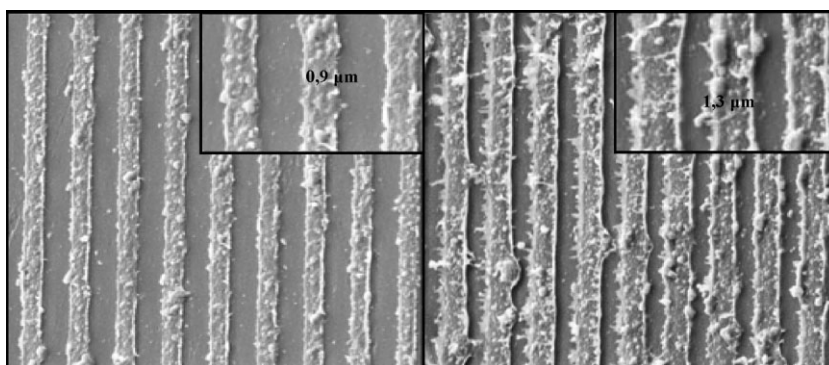


Fig. 2. Dependence of the width of conductive PPy lines with the laser fluence. SEM microscopies laser fluence: (a) 220 mJ cm^{-2} , (b) 72 mJ cm^{-2} .

Results and Discussion

Figure 1 shows WLI images of different PPy structures on polypropylene (PP), obtained by DLIP. The images in Figure 1 suggest that well defined arrays of conductive nanometric structures can be fabricated in one single laser pulse. Figure 1(a) shows line arrays with a period of $3.5 \mu\text{m}$, and regular grid arrays with the same period, fabricate using three beam configuration, Figure 1(b). The pattern is made by local ablation of the conductive polymer at the interference maxima positions, while the conductive polymer remains unaltered at regions with light intensity below a threshold. Also, it can be observed that the width of the lines and their period is very regular.

Figures 2(a) and (b) show SEM microscopies, it can be seen that variations of the laser beam intensity results in a change of the PPy lines width. This effect is quantitatively depicted in Figure 2, the higher the laser fluence the smaller the width of the conductive PPy lines.

Since laser ablation occurs only when a certain laser fluence threshold value is reached,^[20] (that is when the amount of energy deposited by light in the material is enough to cause

polymer decomposition) when low laser fluences is used only a very small part of the light at the interference maxima positions is able to ablate the PPy film [Fig. 2(b)]. As the laser fluence increases, a wider portion of the interference pattern surpasses this threshold energy and wider ablated regions are obtained [Fig. 2(a)]. As a result, the width of the PPy lines decreases.

One important conclusion is that it is possible to tune PPy wire's width by modulation of the laser fluence. Using this configuration, the smallest width of the PPy lines produced without destroying their connectivity was ca. 900 nm .

Another important point is the role of the non-conductive polymer used as substrate during the ablation process. In Figure 3, SEM micrographs of the transversal cuts of the structured PPy films, ablated using 72 mJ cm^{-2} , and their underlying substrates (PP) are shown (platinum layer on the substrates was deposited to protect the polymer surface during milling and to improve the quality of the cuts). As it can be seen only the PPy film is removed at the interference maxima positions. It is clear that PPy is removed but the underlying polymer remains unchanged. There are two

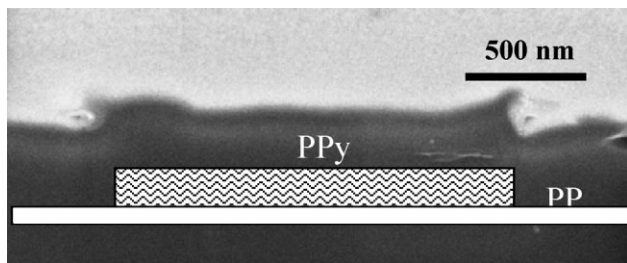


Fig. 3. Cross-sectional analyses of PPy supported onto PP. The figure shows the FIB worked area, the cross-section of the structured polymers, and a scheme with the structuring mechanism in each case. The Pt layer was deposited on the surface to protect the polymer during milling and to improve the quality of the cuts.

reasons: (i) PPy absorbs strongly at 355 nm^[24] while PP (or PE) has negligible absorption at that wavelength,^[25] (ii) PPy is less thermally stable than PP (or PE).^[26,27] The latter effect explains why only the PPy layer is removed, i.e., that the heat deposited by radiation on the PPy is not enough to photothermally remove the PP region closer to the illuminated PPy.

While it is obvious that DLIP is suitable to produce micro/nanometric patterns of PPy in only one single step, it is

important to determine if the remaining conductive polymer has suffered chemical modification during patterning.

The FTIR spectra of the structured PPy/PP and PPy/PE are shown in Figure 4(a) and (b) respectively. The spectrum presents characteristic bands of PPy: 1 550, 1 366, 1 301, 1 169, 1 092, 1 033, 960, 892, 840, 774, 673, and 610 cm⁻¹.^[28] Specifically, bands in the region 1 600–1 800 cm⁻¹, which could be due to > C=O stretching in oxidized products of conductive polymer degradation,^[29] are absent. Consequently, it is possible to conclude that no changes in the chemical structure of the remaining polymer have been produced during the ablation process. A typical UV-vis spectrum of the structured PPy (doped and undoped) is shown in Figure 4(c). Two characteristic bands can be observed: one in the visible at ca. 455 nm and one in the near infrared (NIR) with maximum above 1 100 nm. Since the UV-vis spectrum is directly related to the electronic state of the polymer, the agreement with the spectrum of a doped PPy suggests that the polymer electronic structure is not affected at the non-ablated regions. A related question is if the polymer has redox activity. To test that, the doping/undoping process in the structured PPy is studied. The UV-vis spectrum of the

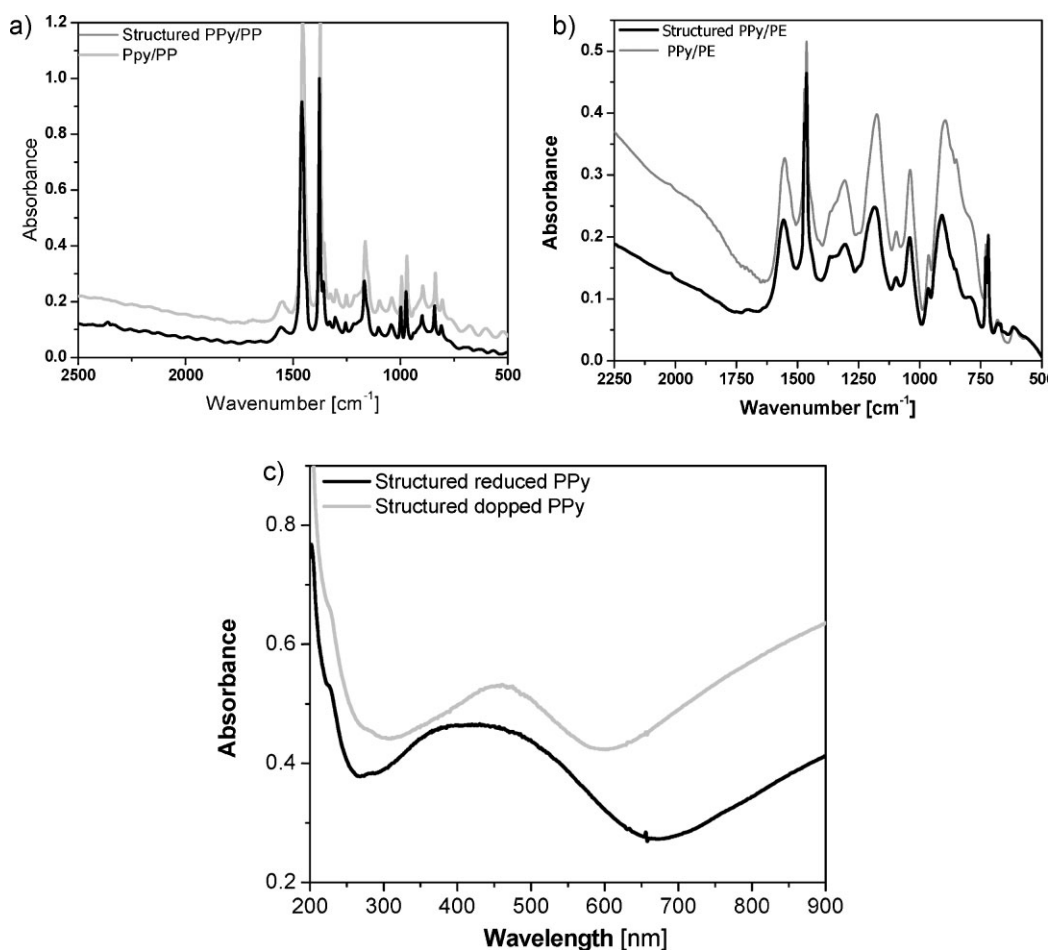


Fig. 4. (a) FTIR spectrum of nanometrically structured PPy films on a PP substrate (black line) and FTIR spectrum of non structured PPy (gray line). (b) FTIR spectrum of nanometrically structured PPy films on a PE substrate (black line) and FTIR spectrum of non structured PPy (gray line). (c) Transmission UV-vis spectrum of a nanometrically structured PPy films on PP substrate: doped (gray line), undoped (black line).



Fig. 5. Photographies of water drop onto PPy nonstructured (a), and structured PPy with lines pattern (0.9 μm wide) (b) and (c) PPy with grid pattern,(period 3.5 μm).

structured and undoped PPy [Fig. 4(c)], produced by treating it with hydrazine solution (1 M, 30 min) shows a typical change on the spectra, a new band appear at ca. 356 nm, the one at 455 nm decreases intensity and the NIR band shifts its maximum to 1 030 nm. The conductivity of the non structured doped PPy, determined by measuring the conductivity of a known section of the film, is 13 (+/-0.2) S cm^{-1} . The structured PPy has a conductivity of 5.7 S cm^{-1} and undoping the polymer, as described before, makes the conductivity decrease to 0.13 (+/-0.2) S cm^{-1} . The values are in agreement with those previously reported for PPy.^[30]

All these results suggest that the chemical and physical properties of PPy remain unaltered at the non ablated regions after DLIP. Besides suggesting that structured PPy remains chemically unaltered, it suggests that PPy arrays retain enough conductivity to give measurable resistances and consequently the conductive PPy arrays produced onto non conductive substrates could be used to produce sensors based on the effect of external media in the electronic properties of the polymer.^[31] In that way, sensors of gases, such as ammonia in air,^[32] can be built. Moreover, the small dimension of the conductive polymer lines would increase the response rate of the devices due to two reasons: (i) mass transport of the analyte to the lines and inside the lines will be enhanced because cylindrical diffusion exists; (ii) the surface/volume ratio is higher for structured films than flat films making that same degree of reaction of the polymer thickness (e.g., 10%) change a larger portion of the wire section. Since the conductive polymers can be modified without affecting the underlying polymer, it would be possible to fabricate sensors receptive to specific ions.^[33]

Wetting Effects

Surface wetting is an important parameter in different phenomena, like cell adhesion and growth,^[34] polymer bonding.^[35] It is known that the wetting does not depend only on the chemical nature of the surface but also on its nano-microtopography of the surface.^[36] On the other hand, the wetting of conductive polymers can be controlled by doping/undoping.^[37] Therefore, it is interesting to measure the wetting of structured PPy. In Figure 5 are shown the images of water drops on flat doped PPy and structured (900 nm wide lines) doped PPy, which can be used to measure the contact angle. As it can be seen the angle of contact changes from ca. 55° for flat PPy to ca. 75° in structured line PPy and 72° for grid

PPy pattern (period 3.5 μm). A similar phenomenon was previously observed with DLIP structured surfaces of conventional polymers.^[38] It seems that the water drop only wets the protruding PPy lines. Therefore air is retained in the gaps between PPy lines making the structured surface more hydrophobic than the flat surface.^[39]

Conclusions

It has been demonstrated that micro/nanometric arrays of lines (as thin as 900 nm) or dots of PPy deposited on dielectric polymers (PP or PE) could be easily fabricated by DLIP at 355 nm. The width of the PPy lines could be controlled by changing the intensity of the laser beam. The conductive PPy arrays retain the chemical and electronic properties of the unstructured surface. On the other hand, the structured PPy shows different wetting than flat PPy layers. Since macroscopic areas can be structured in each laser pulse ($\text{mm}^2\text{-cm}^2$) this process can be easily adapted to produce micro/nanometric patterns on large areas. These investigations may be relevant for the development of high performance materials for polymeric sensors and biological applications.

Experimental

Materials

Pyrrole (Aldrich) was distilled prior to polymerization using reduced pressure. Ammonium persulfate (Aldrich, analytical grade) was used as received from the manufacturer. All aqueous solutions were prepared using twice distilled water. All the other reagents were of analytical quality. PP (20 μm thick) and polyethylene (PE) films (2 μm thick) were purchased from PASA (Argentina).

Synthesis of PPy Supported on PE or PP

PPy was prepared by oxidation of pyrrole (0.1 M) in HCl 1 M with ammonium persulfate (equimolar) as described before.^[22] The reactor was immersed in an ice-water bath to keep the temperatures below 5 °C. In order to produce PPy onto the PP and PE films, squares of 4 cm^2 of each polymer were immersed into the monomer solution. The PE or PP films were previously oxidized by immersion in sulfochromic solution, followed by thorough washing.^[a] After the finalization of the reaction, the films of PPy supported onto PP and PE were washed in an ultrasonic bath for 15 min to ensure that no reactant is retained in the film.

^aIt was found that untreated PE or PP substrate show incomplete wetting by the polymerization solution, leading to non uniform PPy film deposition.

DLIP Experiments

A Q-switched Nd:YAG laser (Spectra Physics Brilliant Blue) with a frequency of 10 Hz and pulse duration of 5–10 ns was used for the interference experiments. The laser beam was split into two or three sub-beams which were guided by mirrors to interfere on the sample surface to produce line and grid arrays respectively. The period of the line pattern was 3.5 μm and the utilized wavelength was 355 nm. All the samples were structured using a single laser pulse.

White Light Interferometry (WLI)

The depth and period of the micropatterns were characterized using a white light interferometer (New View 200 3-D Imaging Surface Structure Analyzer, Zygo Corporation, USA).

Spectroscopy

Fourier transform infrared spectroscopy (FTIR): IR-spectra of structured PPy supported onto non conducting polymers were performed by transmission using a Bruker Tensor 27 FT-IR spectrometer. The supported line-arrays were dried under vacuum prior to measurement. The spectrum shows a combination of the base polymer (2 μm thick PE) and PPy.

Cross-Sectional and Chemical Analysis

All samples were imaged with a high-resolution SEM equipped with a field emission gun (FEI Strata DB 235) at 5 kV acceleration voltage. For cross-sectional analysis, a dual beam workstation (FEI Strata DB 235) using the electron beam for imaging and Pt deposition and the focused ion beam (Ga) for milling of the sample was employed. X-ray spectrometry (EDX) was carried out at 5 kV of acceleration voltage.

Electrical Conductivity Measurements

The electrical resistance of the films, before and after structuring, deposited onto a non conductive polymer, was determined by the four probe method using an HP5532A high precision voltmeter. The thickness of the films, necessary to calculate the conductivity was estimated from the cross-sections made using FIB.

Contact Angle Measurements

The measurements were carried out at 25 °C, using 5 μl of bidistilled water deposited onto the surface. A microscope Intel Play QX3 with 60× objective was used for photographing the drop image. The images (jpeg format) were analyzed using "Drop Analysis", an add-in of ImageJ image processing software.^[23]

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- [1] A. Guiseppi-Elie, G. Wallace, T. Matsue, *Handbook of Conducting Polymers*, 3rd Edn (Eds: T. A. Skotheim, J. Reynolds), CRC, New York, USA 2007.
- [2] L. Xu, J. Wang, Y. Song, L. Jiang, *Chem. Mater.* **2008**, *20*, 3554.
- [3] E. Smela, *Adv. Mater.* **2003**, *15*, 481.
- [4] L. Xu, W. Chen, A. Mulchandani, Y. Yan, *Angew. Chem, Int. Ed.* **2005**, *44*, 6009.

- [5] G. Cho, M. Jung, H. Yang, B. Lee, J. H. Song, *Mater. Lett.* **2007**, *61*, 1086.
- [6] N. Gomez, Y. Jae, J. Lee, D. Nickels, C. E. Schmidt, *Adv. Funct. Mater.* **2007**, *17*, 1645.
- [7] P. M. George, A. W. Lyckman, D. A. LaVan, A. Hedge, Y. Leung, R. Avasare, C. Testa, P. M. Alexander, R. Langer, M. Sur, *Biomaterials* **2005**, *26*, 3511.
- [8] C. E. Schmidt, V. R. Shastri, J. P. Vacanti, R. Langer, *Proc. Natl. Acad. Sci.* **1997**, *94*, 8948.
- [9] R. L. Williams, P. J. Doherty, *J. Mater. Sci. Mater. Med.* **1994**, *5*, 429.
- [10] S. J. Chen, D. Y. Wang, C. W. Yuan, X. D. Wang, P. Zhang, X. S. Gu, *J. Mater. Sci. Lett.* **2000**, *19*, 2157.
- [11] J. Y. Yang, D. C. Martin, *Sens. Actuators, B.* **2004**, *101*, 133.
- [12] G. Shi, M. Rouabhia, Z. Wang, L. H. Dao, Z. Zhang, *Biomaterials* **2004**, *25*, 2477.
- [13] D. H. Kim, M. Abidian, D. C. Martin, *J. Biomed. Mater. Res. A.* **2004**, *71*, 577.
- [14] X. Cui, V. A. Lee, Y. Raphael, J. A. Wiler, J. F. Hetke, D. J. Anderson, D. C. Martin, *J. Biomed. Mater. Res.* **2001**, *56*, 261.
- [15] T. Diepold, E. Obermeier, Berchtold, *J. Micromech. Microeng.* **1998**, *8*, 144.
- [16] Y. Xia, G. M. Whitesides, *Angew. Chem, Int. Ed. Engl.* **1998**, *37*, 551.
- [17] M. Hecke, W. K. Schomburg, *J. Micromech. Microeng.* **2004**, *14*, 1.
- [18] A. F. Lasagni, D. F. Acevedo, C. A. Barbero, F. Mucklich, *Pol. Eng. Sci.* **2008**, *48*, 2367.
- [19] A. F. Lasagni, D. F. Acevedo, C. A. Barbero, F. Mucklich, *Adv. Eng. Mater.* **2007**, *9*, 99.
- [20] A. F. Lasagni, D. F. Acevedo, C. A. Barbero, F. Mucklich, *Adv. Mater.* **2007**, *19*, 1272.
- [21] A. F. Lasagni, D. F. Acevedo, C. A. Barbero, F. Mucklich, *Appl. Phys. A.* **2008**, *91*, 369.
- [22] K. C. Khulbe, R. S. Mann, C. P. Khulbe, *J. Pol. Sci.: Polym. Chem. Ed.* **1985**, *20*, 1089.
- [23] <http://rsbweb.nih.gov/ij/>
- [24] E. Håkansson, T. Lin, H. Wang, A. Kaynak, *Synth. Met.* **2006**, *156*, 1194.
- [25] M. I. Khalil, G. M. Nasr, N. M. El-Sawy, *J. Phys. D: Appl. Phys.* **2006**, *39*, 5305.
- [26] K. Cheaha, M. Forsyth, V. T. Truong, C. Olsson-Jacques, *Synth. Met.* **1997**, *84*, 829.
- [27] J. Golebiewski, A. Galeski, *Compos. Sci. Technol.* **2007**, *67*, 3442.
- [28] S. Ghosh, G. A. Bowmaker, R. P. Cooney, J. M. Seakins, *Synth. Met.* **1998**, *95*, 63.
- [29] *Infrared Characteristic Group Frequencies*, 3rd Edn (Eds: G. Socrates), J. Wiley & Sons Ltd, West Sussex, England 1994.
- [30] J. Aguilar-Hernández, K. J. Potje-Kamloth, *Phys. D: Appl. Phys.* **2001**, *34*, 1700.
- [31] L. Xia, Z. Wei, M. Wan, *J. of Colloid and Interface Sci.* **2010**, *1*, 1.
- [32] S. Carquigny, J. B. Sanchez, F. Berger, B. Lakard, F. Lallemand, *Talanta* **2009**, *78*, 199.

- [33] D. F. Acevedo, J. M. Balach, C. R. Rivarola, M. C. Miras, C. A. Barbero, *Faraday Discuss.* **2006**, 131, 235.
- [34] E. A. Vogler, *Biophys. J.* **1988**, 53, 759.
- [35] S. Wu, *Polymer Interface and Adhesion*, 1st Edn, CRC Press, New York, USA **1982**.
- [36] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, 40, 546.
- [37] J. Isaksson, N. D. Robinson, M. Berggren, *Thin Solid Films* **2006**, 515, 2003.
- [38] D. Acevedo, G. Martinez, J. Toledo, E. Arana, F. Yslas, C. Mucklich, H. Barbero, J. Salavagione, *J. Phys. Chem. B* **2009**, 113, 14661.
- [39] Jung Yong Chae, B. Bhushan, *Nanotechnology* **2006**, 17, 4970.
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