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Smart hydrogels for Novel Optical Functions

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Summary: Nanocomposites of inherently conductive polyaniline (PANI) within a highly hydrophilic polyvinyl alcohol (PVA) based hydrogel have been produced by coupling a conventional dispersion chemical oxidative polymerization to a subsequent high energy irradiation step, in order to convert the polymer stabilizing the aqueous dispersion, namely the PVA, into a highly water swollen hydrogel incorporating the PANI particles. The incorporation of the electroactive and ''pH-sensitive'' polymer into a transparent and highly permeable hydrogel matrix has been pursued as a route to the development of a novel class of potentially biocompatible, smart hydrogels that can respond to changes of the surrounding environment with measurable changes in their optical properties. Absorption spectra show that the optical absorption bands typical of PANI, known to be reversibly affected by changes of the polymer oxidation state or pH or both, are well preserved in the PVA hydrogels. Even more interestingly, fluorescence is observed from the nanoparticles of PANI in its inherently conductive form, whose intensity is strongly affected by changes of pH. This has enhanced the importance of this material to a large extent from both a scientific and a practical point of view.

Keywords: conducting polymers; fluorescence; hydrogels; irradiation; UV-vis spectroscopy

Introduction

Polyaniline is a mixed oxidation state polymer composed of reduced benzenoid units and oxidized quinoid units. It can exist in different oxidation states ranging from the completely reduced, colorless leucoemeraldine base state (LB) to the completely oxidized, violet pernigraniline base (PB) state. These two forms are both insulating. The half oxidized, blue emeraldine base state is a semiconductor and is composed of an alternating sequence of two benzenoid units and one quinoid unit. Emeraldine base (EB) can be transformed into the conductive, green emeraldine salt (ES) by acid doping reactions. This process is a non-redox doping where the imine nitrogen atoms of the polymer are protonated to give a polaronic form where both spin and charge are delocalized along the entire polymer backbone (see Scheme 1).[1,2] Of course, the emeraldine salt can be reverted to the ''undoped'' base form by a treatment with an alkali.

Polyaniline (PANI) has been the subject of extensive investigations owing primarily to its great application potential in electronics, industry and medicine, e.g. in fuel cells, electrochromic displays, sensors and biosensors, actuator components in microsurgical tools, corrective implantable aids, nerve repair conduits, artificial muscles, etc.[3–4] Beside the electronic properties, these seemingly ubiquitous applications of PANI are due to some other important properties, such as its good environmental

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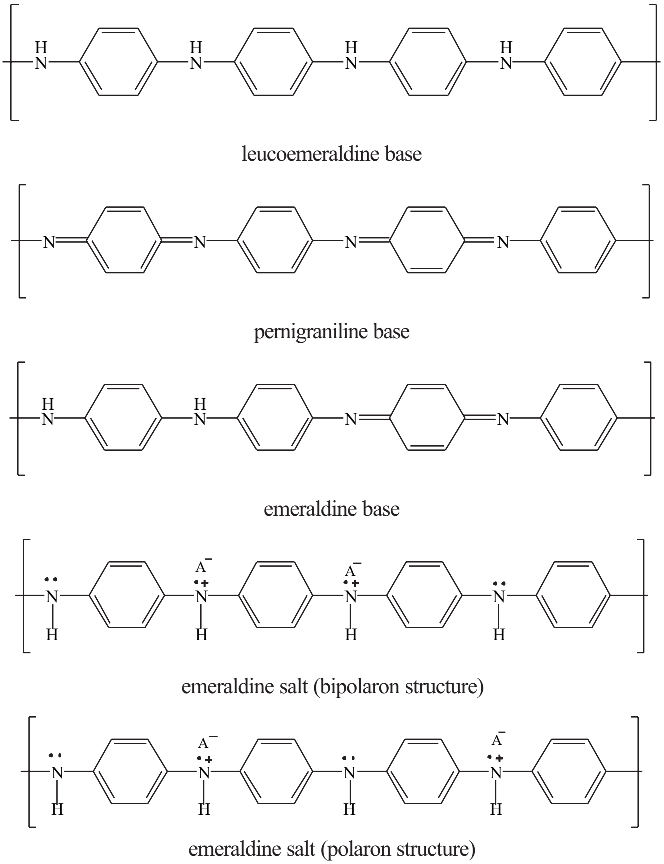

Scheme 1.
Repetitive units of the different forms of polyaniline.

stability, relative easy of synthesis, low cost and, finally, structure-process-property flexibility by design, i.e. by means of suitable co-polymerization or incorporation as a dispersed phase into other stabilizing materials. Incorporating PANI into other polymers has been often attempted to overcome the major problems of PANI associated with its use and related to its very fragile structure and poor solubility, especially in the conductive form, giving rise to processing difficulties. There are two general approaches to the preparation of PANI composites. One technique involves physical blending the conducting polymer with a stabilizing polymer;[5] another possibility involves the polymerization ''in situ'' the conducting polymer onto or within another polymer.[6–7] Often the matrix polymer has insulating electrical properties, so it detrimentally affects the electrical conductivity of the composite.[8–9]

Further to that, it has been observed that there are significant differences in electrical and optical properties of PANI depending on how it has been synthesized or even processed after synthesis. Films cast from PANI-EB powder, dissolved in N-methylpyrrolidone (NMP), displayed different conductivity relaxation time distributions than the pristine powders. Even more interestingly, unexpected properties, such as the emission of white light from polyaniline cast into films from solutions, has been observed in both the emeraldine base and the leucoemeraldine base states, when they were used as the emitting layer of a light emitting diode. The fact that the fully reduced LB form of PANI exhibited electro-luminescence was not surprising, since PANI-LB was already proved to exhibit photoluminescence in both the solid sate and in solution, but electro-luminescence of the EB form was quite unexpected. In fact, there is general agreement on the fact that the benzenoid units in polyaniline are responsible for fluorescence, while the quinoid units actually act as excitation traps, quenching the photoluminescence produced by the benzenoid units. This ‘‘exceptional’’ behavior of the EB films was attributed to the presence of a ‘‘phase segregated’’ structure in the film, with regions where only oxidized quinoid units or only reduced benzenoid units were concentrated.[1,10] Evidence of photoluminescence from the emeraldine salt is provided by the work of Gong *et al.*,[11–12] who report fluorescence to be exhibited by PANI-ES when the polymer is produced at low temperature through a solid–state synthesis method using an heteropoly acid (a solid-state acid). The authors justify this behavior as a result of a high degree of order in the macromolecular chains orientation, thus providing the rigidity and the coplanarity that should enable fluorescence. Processability of this highly rigid form of PANI is doubtful.

In this paper, the results of UV-visible absorption and fluorescence spectroscopy is reported with reference to a novel family of PANI composite materials, where PANI nanoparticles are dispersed into a hydrogel matrix. The synthesis of nanocomposites was performed via a two step process: (i) ‘‘in situ’’ polymerization of aniline in the presence of a steric stabilizer, namely polyvinyl alcohol (PVA), followed by (ii) γ-irradiation of the so obtained PANI dispersions, in order to induce chemical cross-linking to the steric stabilizer.[13,14] In an earlier advancement of this research, morphological analysis, carried out by both scanning electron microscopy and atomic force microscopy, proved that PANI was synthesized in the form spherical particles with diameter of about 10nm.[14] The evidence of fluorescence signals in the PANI-ES dispersions, as obtained after step (i), using PVA as steric stabilizer, was also reported for the excitation wavelength of 290 nm. This paper documents the first evidence of fluorescence signals of PANI-ES nanoparticles dispersed into another polymer, although slightly peculiar, considering the large amount of water incorporated (approx. 96 wt%) in the hydrogel matrix.[13] Furthermore, the development of a conductive polymer-hydrogel composite may be considered as a part of a general ‘‘nanocomposite’’ functional hydrogels platform that may offer some specific advantages: (i) it can address the problem of conjugated oligomers and polymers poor processability, without impairing conductivity due to the intrinsic conductivity of the water swollen matrix; (ii) the physical and mechanical properties of the composite may be varied from a soft and spreadable paste to a tough and flexible membrane, by tuning the matrix crosslinking degree and density; (iii) the hydrogel matrix can be transparent, thus it can only minimally interfere with the optical and electro-optical properties of the conductive polymer; (iv) the hydrogel matrix can ensure high permeability to gases, vapors and liquids, therefore, it can be regarded as a good vehicle of doping agents; (v) biocompatibility of devices can be pursued starting from using a biocompatible active material, in a typical bottom-up approach.

Experimental Part

PANI aqueous dispersions have been obtained by chemical oxidation of an acid solution of aniline using ammonium persulphate as redox initiator and PVA ($M_w = 47{,}000$, degree of hydrolysis 88) as steric stabilizer. Details of the synthetic procedure are reported elsewhere.[13] Absence of aniline within the dispersions was assessed by both high performance liquid chromatography (HPLC) and gas chromatography (GC).

Before irradiation, dispersions were diluted tenfold with the steric stabilizer/water solution (at 4% wt), already used to prevent macroscopic precipitation of PANI during polymerization, so that stabilizer weight concentration was kept constant. Hydrogel composites were obtained by ^{60}Co γ-irradiation of the diluted dispersions of synthesized PANI. Irradiation was performed in glass vials under nitrogen at a dose rate of 1,6 kGy/h and a total absorbed dose of 80 kGy. During irradiation, temperature was maintained at 10 °C. Hydrogels of pure PVA were also produced in the same conditions for comparison.

Water content on hydrogels at their original pH, measured gravimetrically, was of about 96 wt%, while the amount of PANI in the hydrogels was approximately 0.06 wt%.

The original pH of hydrogels containing PANI was equal to 1.6 and was brought to 2.5, 4.5, 7.4 and 9.3 by equilibrating the hydrogels with phosphate buffer solutions all having almost constant ionic strength (0.20–0.25 mol/l). Pure PVA hydrogels were also equilibrated at the five different pHs using the same buffers as for the hydrogel nano-composites, except for that obtained at pH = 1.6, that was obtained by immersing the hydrogel into a hydrochloric acid aqueous solution having the same ionic strength of the buffers by addition of sodium chloride. After immersion in the buffer solutions, the excess surface liquid was removed from the hydrogels by centrifugation for 2 min at 2000 rpm.

While pure PVA hydrogels were transparent and colorless, PANI/PVA hydrogels at pH 1.6, 2.5 and 4.5 showed a transparent, dark-green color, while at pH 7.4 and 9.3 they turned into dark-blue, always maintaining transparency. It is worth mentioning that after being immersed for up to two weeks into the different pH buffer solutions no hydrogel samples discolored, as well as no buffer solutions turned colored, thus suggesting that the PANI nanoparticles were tightly bound to their hydrogel network.

Hydrogels were smeared on a 0.5 mm demountable quartz couvette and absorption and emission spectra were performed on the same sample.

Absorption spectra were carried out by using a Jasco V-570 Spectrophotometer (scan speed 40 nm/min integration time 2 sec, bandwidth 1 nm) at room temperature. Hydrogels were smeared on a 0.5 mm demountable quartz couvette.

Fluorescence measurements were carried out in backscattering configuration at room temperature, with a Jasco FP-6500 spectrofluorimeter, equipped with a Xenon lamp (150 W).

The emission spectra, at different excitation wavelengths, in the range 240–700 nm, were obtained with emission and excitation bandwidth of 3 nm, scan-speed of 100 nm/min and integration time of 1 s. The experimental errors were about 5%.

Results and Discussion

Figure 1 shows UV-visible absorption spectra of PANI/PVA hydrogel composites at five different pHs

The composites present the distinctive features of the UV-visible spectra of PANI containing systems: absorption peaks in the (i) 300–350 nm region and in the (ii) 550–800 nm region.[15–19] It is worth noting that pure PVA hydrogels at all pHs do not show any significant absorption band in the 400–980 nm region, as clearly visible in the inset of Figure 1, where the absorption spectrum for the PVA hydrogel at pH 2.5 is reported for comparison.

The HCl doped emeraldine salt, present in the hydrogels at pH 1.6, 2.5 and 4.5, contributes with the characteristic absorption bands at *about* 340 nm in region (i) and at 820 nm wavelength in region (ii), which are due to the π–π^* transition of benzenoid rings (associated with the reduced benzenoid repeat units) and the formation of a polaron structure, respectively. In addition, ES also shows a third band at 430 nm, due to the formation of the doping level owing to the exciton transition, caused by interband

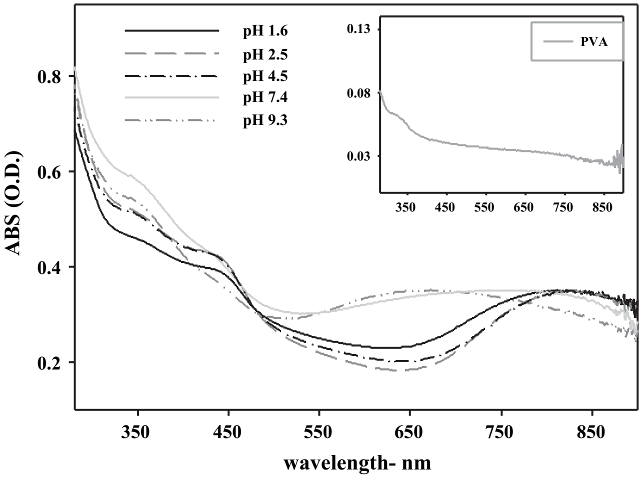

Figure 1.
UV-Vis absorption spectra of PANI/PVA hydrogel composites at the different pHs of the hydrogel swelling medium. Inset: spectrum of the pure PVA hydrogel.

charge transfer from the benzenoid to the quinoid moieties of the protonated PANI (polaron/bipolaron transition).[15]

At the other extreme of the pH range investigated (i.e. pH = 9.3) the absorption band in region (i) is practically unmodified and a new band in region (ii) appears, at about 670 nm, attributable to the benzenoid to quinoid exciton transition (BQET), whereas both absorptions at 430 nm and 800 nm are no longer present. The value for the BQET is reported to be highly influenced by the specific arrangements of the polymer chains[16] and, for example, while EB in solution presents absorptions that can be centered between 620–634 nm, EB films can display a positioning of the band peak in the 620–666 nm interval depending on the processing conditions.[1,10,17,18] Despite of the high value of pH reached, from the positioning of the absorption bands that PANI it is evident was not converted into the fully oxidized, pernigraniline form, as this should have brought the characteristic absorption band in region (ii) down to about 560 nm.[17]

The contribution of PANI to the nanocomposite absorptions at pH 7.4 actually present both features of the protonated emeraldine and the emeraldine base: the band at 340 nm is always present, as expected; an attenuated absorption at 420 nm, slightly blue shifted with respect to that observed at acidic pHs, is also visible and a broad absorption band in region (ii), with a maximum at 780 nm, which looks like the merge of the two bands at 800 nm and 670 nm, already observed at the two extreme pHs of the investigated range. It may be that some degree of doping survives in PANI also at the neutral pH, this effect being probably due to a strong interaction of the synthesized polyaniline with polyvinyl alcohol, through grafting of PANI chains on PVA backbone and/or the possibility of formation of hydrogen bonding between the –OH groups of PVA and the =N–H or the –NH– groups of PANI.[19] The H-bonding, in particular, should be disrupted at the alkaline pH.

In Figure 2 the photoluminescence spectra obtained at an excitation wavelength of 290 nm for the PANI/hydrogel nanocomposite at its original pH and for the corresponding pure PVA hydrogel at the same pH are reported. It can be observed that, whilst PVA doesn't show any significant emission band the composite containing PANI shows a distinct emission band peaked at about 330 nm. The specific features of the observed emission band are visible in the 3D-plot depicted in Figure 3

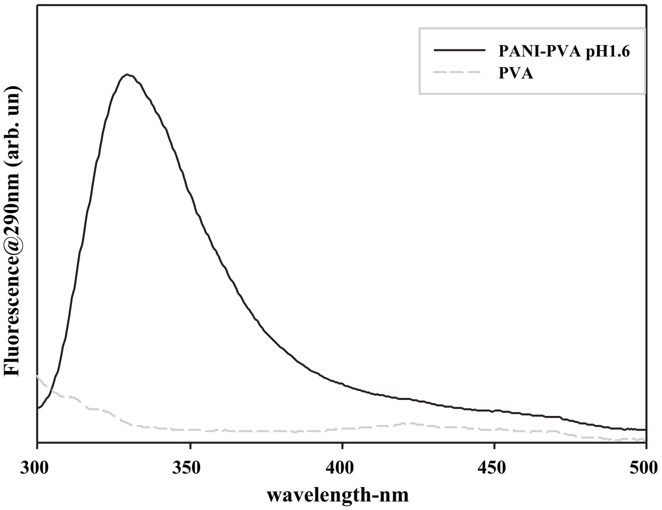

Figure 2.
Fluorescence of PVA hydrogel and PANI/PVA hydrogel composite at pH = 1.6 at the excitation wavelength of 290 nm.

where the fluorescence intensity is diagramed as function of both the excitation and emission wavelengths. The emission band is quite broad but it is detectable with excitation wavelengths in a quite narrow interval (260 nm–310 nm). This band could be attributed to one component of ''benzenoid'' band in the UV range.

In Figure 4 the influence of pH on the photoluminescence spectra and, in the inset, the maximum emission intensity as function of pH are reported. The

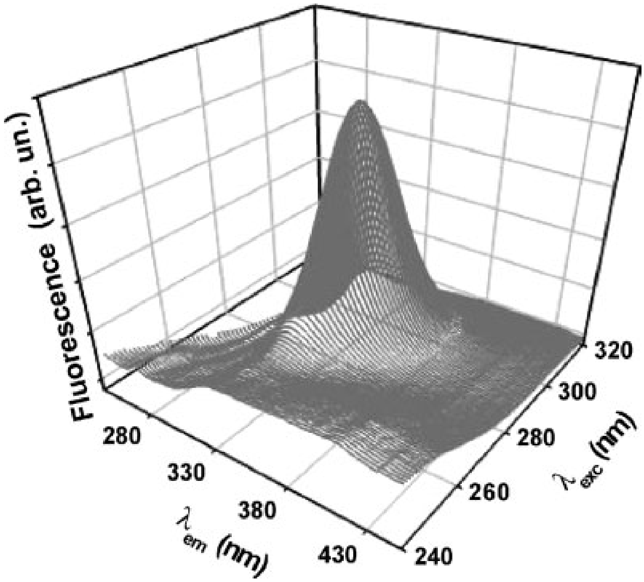

Figure 3.
Fluorescence of PANI/PVA hydrogel composite at pH = 1.6. Spectra were recorded at 1nm excitation wavelength intervals in the 240–320 nm range.

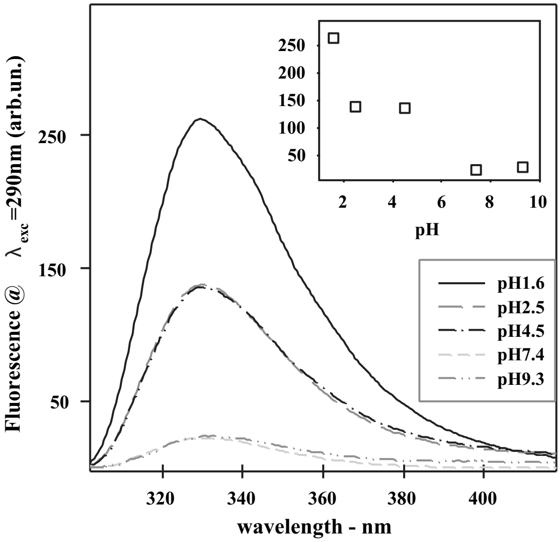

Figure 4.
Fluorescence spectra of PANI/PVA hydrogel composites at the different pHs of the hydrogel swelling medium and for the excitation wavelength of 290 nm. Inset: intensity at λ_{max} as function of pH.

fluorescence band does not change the λ_{max} position with pH, but the emission intensity decreases by increasing pH. This is quite an unexpected result as at the best of our knowledge there is not evidence in literature for the emission of PANI-ES dispersions. Furthermore, there is a general agreement on the concept that the photoluminescence of polyaniline is a result of the reduced benzenoid units, and in facts it has been observed for LB, but is quenched in ES due to HCl doping, which occurs at the top of the valence band.[20]

Also the optical characterization carried out by the same authors onto an analogue PANI/hydrogel composite system which uses polyvinyl pyrrolidone (PVP) as a polymeric stabilizer for the PANI dispersion did not present emission bands at the three pH investigated, namely 4, 7 and 9, despite of the fact that absorption spectra were at all similar than those here reported for the PVA based hydrogels.[14] Therefore, the chemical structure of the polymeric stabilizer and, in turn, of the parent hydrogel plays a major role in affecting the photoluminescence behavior of the PANI/hydrogel composites, as well as it was proved that it strongly affects the morphology of the thin films obtained by spinning and air drying the produced dispersions. In particular, the dispersions obtained using PVP presented a strong tendency of the single nanoparticles produced into aggregation into needles of hundred of nanometers length. Conversely, PVA stabilized dispersions presented in the thin films individual particles of approximately 10 nm diameter.[14] Further investigations are undergoing to better elucidate relationships between the observed photoluminescence phenomena and the structural and morphological properties of PANI in this particular environment.

Conclusions

The two step synthesis of PANI/PVA hydrogels has made a successful stride towards the development of a novel class of nanocomposite functional hydrogels with interesting optical properties. The UV-vis absorption spectra of the hydrogels present all the characteristic features of aqueous PANI systems with absorption bands both in the UV and visible region of the spectrum, this last being affected by both the oxidation state and the doping level of PANI. Photoluminescence of the PANI-ES form is observed, whose intensity is affected by the pH of the hydrogel swelling medium and, therefore, by the doping level of polyaniline. Whether the key to have fluorescence properties is to get a phase segregated structure at an interface or to obtain individual, reciprocally non-interacting nanoparticles or strong interactions with the suspending polymer (PVA), it is clear though that the synthetic method for making the PANI composite can strongly affect the composite material properties. Further understanding and optimizing the fluorescence parameters could help in the designing of novel optical sensors based on this class of conducting polymer/hydrogel nanocomposites.

[1] J. Y. Shimano, A. G. MacDiarmid, *Synth. Met* **2001**, *123*, 251.

[2] P. Ghosh, S. Siddhanta, A. Chakrabarti, *European Polym. J.* **1999**, *35*, 699.

[3] A. Pron, P. Rannou, *Prog. Polym Sci.* **2002**, *27*, 135.

[4] B. Adhikari, S. Majumdar, *Prog. Polym Sci.* **2004**, *29*, 699.

[5] A. Pud, N. Ogurtsov, A. Korzhenko, G. Shapoval, *Polym Sci.* **2003**, *28*, 1701.

[6] M. Wan, M. Li, J. Li, Z. Liu, *Thin Solid Films* **1995**, *259*, 188.

[7] E. Ruckenstein, Y. Sun, *Synth. Met.* **1995**, *74*, 107.

[8] O. T. Ikkala, J. Laakso, V. Vakiparta, E. Virtanen, H. Ruohonen, H. Jarvinen, T. Taka, P. Passiniemi, J. E. Osterhom, Y. Cao, A. Andreatta, P. Smith, A. J. Heeger, *Synth. Met.* **1995**, *69*, 97.

[9] R. K. Paul, C. K. S. Pillai, *Synth. Met.* **2000**, *114*, 27.

[10] S. A. Chen, K. R. Chuang, C. I. Chao, H. T. Lee, *Synth. Met.* **1996**, *82*, 207.

[11] J. Gong, J. Yu, Y. Chen, L. Qu, *Materials Letters* **2002**, *57*, 765.

[12] J. Gong, X. J. Cui, Z. W. Xie, S. G. Wang, L. Y. Qu, *Synth. Met.* **2002**, *129*, 187.

[13] C. Dispenza, C. Lo Presti, C. Belfiore, G. Spadaro, S. Piazza, *Polymer* **2006**, *47*, 961.

[14] C. Dispenza, M. Leone, C. Lo Presti, F. Librizzi, G. Spadaro, V. Vetri, *Journal of Non-Crystalline Solids*, in press.

[15] P. M. McManus, S. C. Yang, R. J. Cushman, *J. Chem. Soc., Chem. Comm.* **1985**, 1556.

[16] O. P. Dimitriev, *Synth. Met.* **2002**, *125*, 359.

[17] J. E. Albuquerque, L. H. C. Mattoso, D. T. Balogh, R. M. Faria, J. G. Masters, A. G. MacDiarmid, *Synth. Met.* **2000**, *113*, 19.

[18] J. E. Albuquerque, L. H. C. Mattoso, R. M. Faria, J. G. Masters, A. G. MacDiarmid, *Synth. Met.* **2004**, *146*, 1.

[19] R. Gangopadhyay, A. De, G. Ghosh, *Synth. Met.* **2001**, *123*, 21.

[20] M. K. Ram, G. Mascetti, S. Paddeu, E. Maccioni, C. Nicolini, *Synth. Met.* **1997**, *89*, 63.