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Poly(acrylic acid)-guided synthesis of helical polyaniline microwires

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Abstract

We present a facile method to prepare helical polyaniline (PANI) microwires or rods guided by poly(acrylic acid) (PAA). The average length and diameter of the helical strands were about 3.5 μm and 500 nm, respectively. The pitch distance was about 400 nm. The morphology of the helical PANI microwires was affected by the concentration of PAA. As the concentration was decreased to below 0.05 mg/ml, helical wire- or rod-like products were observed. The structure of the helical polyaniline microwires were characterized by means of TEM, SEM, XRD, FTIR and UV–vis spectroscopy.

Keywords: Helical; Polyaniline; Microwires

1. Introduction

Polyaniline (PANI) is one of the most important conducting polymers because of its good processibility, environmental stability, and its oxidation- or protonation-adjustable electrooptical properties [1,2] as well as its potential for a variety of applications [3,4]. In the past years, many one-dimensional (1-D) polyaniline structures including nanowires, rods, and tubes have been studied with the expectation that such materials will have the advantages of both low-dimensional systems and organic conductors [5]. The synthesis of polyaniline with 1-D nanostructures has been achieved with the aid of either a hard template, such as zeolite channels [6], track-etched polycarbonate [7,8] and anodized alumina [9], or a soft template, such as surfactants [10], micelles [11–13], liquid crystals [14], thiolated cyclodextrins [15], and polyacids [16]. Electrochemical methods [17,18] and physical methods, such as electrospnning [19,20] and mechanical stretching [21], have also been used to make polyaniline nanofibers. Recently, interfacial polymerization, oligomer-assisted and nanofiber seeding method were also used to synthesize PANI nanofibers [22–24].

In the traditional method to prepare PANI–polyacid complexes, polyacids, such as poly(acrylic acid) (PAA) and poly(styrene sulfonic acid), have been used as dopants to obtain conducting PANI [16,25,26]. The method consists of dissolving the aniline monomer in a large amount of polyacid, followed by oxidative polymerization of the monomer. Among PANI–polyacid complexes, PANI–PAA has been studied quite extensively [27,28]. The morphology of PANI–PAA film shows the presence of small clusters resembling those of conventional PANI film and large globular-like conglomerates [27]. Fibrilar network morphology of PANI–PAA can be obtained by using *N*-methyl-2-pyrrolidinone (NMP) as solvent [28]. Colloidal polyaniline fibrils were made by template guided chemical polymerization [16]. As we all know, helical polymers have been attracted more attentions in the past few years [29,30]. And helical PANI induced by specific interaction with biomolecules or using synthetic lipid assemblies as a template was obtained [31,32]. Water-soluble chiral PANI–PAA nanocomposites have also been fabricated by using an enantiomerically pure camphorsulfonic acid (CSA) as chiral inducing agent and poly(acrylic acid) as template [33,34]. Up to date, very little has been reported on helical morphology of PANI–PAA nanowires.

In this paper, we present a successful facile synthesis of

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PANI–PAA complex with helical nanostructures via a simple template-guided polymerization of aniline with low molecular poly(acrylic acid) ($M_n \sim 1000$) as the template. The synthesis has been achieved in two steps. Firstly, aniline monomers (ANI) were adsorbed, through electrostatic and/or hydrogen bonding interactions, onto poly (acrylic acid) to form an adduct $(ANI)_x/PAA$ in aqueous solution. Then an oxidant, ammonium persulfate (APS), was added to polymerize the adsorbed aniline monomers to afford a doped interpolymer PANI–PAA complex. During the polymerization, the interpolymer complexes form PANI microwires or rods as guided by the extended chains of PAA as illustrated in Fig. 1.

2. Experimental

2.1. Chemicals

Aniline monomer was distilled under reduced pressure and stored below 0 °C. Poly(acrylic acid) (30% aqueous solution) (Tianjin Kermel Chemical Reagent Development Center). All the other reagents were analytical grade, and used without further purification, including ammonia persulfate (APS) (Aldrich), methanol (Beijing Chemical Factory) and other reagents.

2.2. Equipment

Scanning electron microscopy (SEM) measurements were performed on a SHIMADZU SSX-550 microscope. Transmission electron microscopy (TEM) experiments were performed on a Hitachi S-570 microscope with an acceleration voltage of 200 kV. IR Spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR22 Spectrometer. X-ray diffraction patterns (XRD) were obtained with a Siemens D5005 diffractometer using Cu K_α radiation. UV/vis spectra were recorded on a UV-2501 PC Spectrometer (SHIMADZU).

2.3. Preparation of helical polyaniline microwires

In a typical polymerization of PANI/PAA microwires/rods with helical structures, 0.28 g aniline and 0.010 g PAA were dissolved in 30 ml deionized water with stirring at room temperature. The mixture was then cooled to about 0–5 °C in an ice bath, followed by addition of 2 ml of ammonium persulfate (0.684 g) aqueous solution as an oxidant. The mixture was allowed to react for 15 h, and then filtered. The residue was washed with water and methanol several times, and finally dried under a dynamic vacuum at room temperature for 24 h.

3. Results and discussion

3.1. Morphology and mechanism

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology of PANI–PAA complexes. As shown in Fig. 2, SEM revealed that most of the materials have wire-like or rod-like structures. The diameters of the wires are about 200 and 500 nm. The concentration of PAA was found to strongly affect the PANI–PAA morphology. When the PAA concentration was higher than 0.5 mg/ml, no wires or rods were observed. As the concentration was decreased to below 0.1 mg/ml and as low as 0.001 mg/ml, wire- or rod-like products were observed. More interestingly, the lower the concentration of PAA, the more the wire- or rod-like product formed. TEM images also showed that there were relatively straight wire- or rod-like structures. But to our surprise, some of the wires/rods were found to have helical nanostrucutres that are clearly identifiable in the TEM images (Fig. 3). The diameter of the helical strands was about 500 nm. The pitch distance was about 400 nm.

In an effort to elucidate the mechanism for the helical nanostructure formation process, TEM images of PANI–PAA at different PAA concentrations in the synthesis under optimal conditions were measured and are shown in Fig. 3.

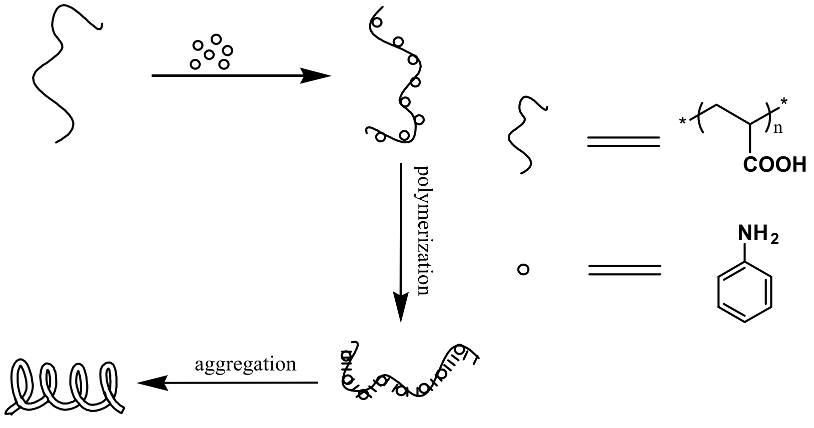

Fig. 1. Simplified schematic representation of PAA-guided synthesis PANI microwires.

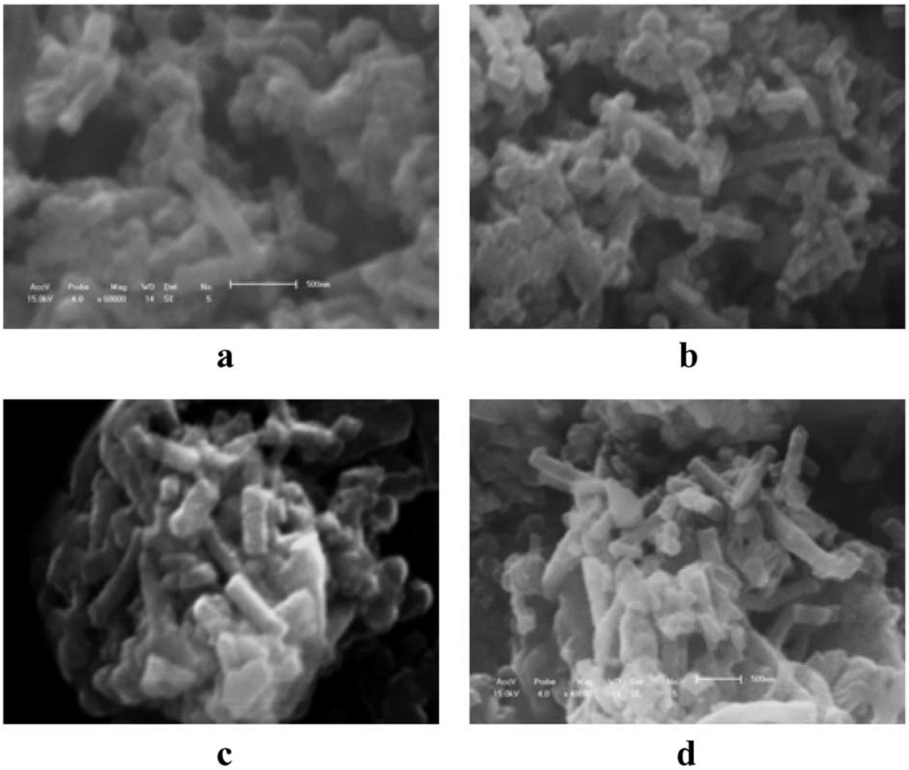

Fig. 2. SEM images of PANI–PAA synthesized under different concentration of PAA. (a) [PAA] = 0.1 mg/ml; (b) [PAA] = 0.05 mg/ml; (c) [PAA] = 0.02 mg/ml; (d) [PAA] = 0.005 mg/ml; synthetic conditions: aniline = 0.1 mol/l, aniline/APS = 1, reaction time = 14 h, temperature = 0 °C.

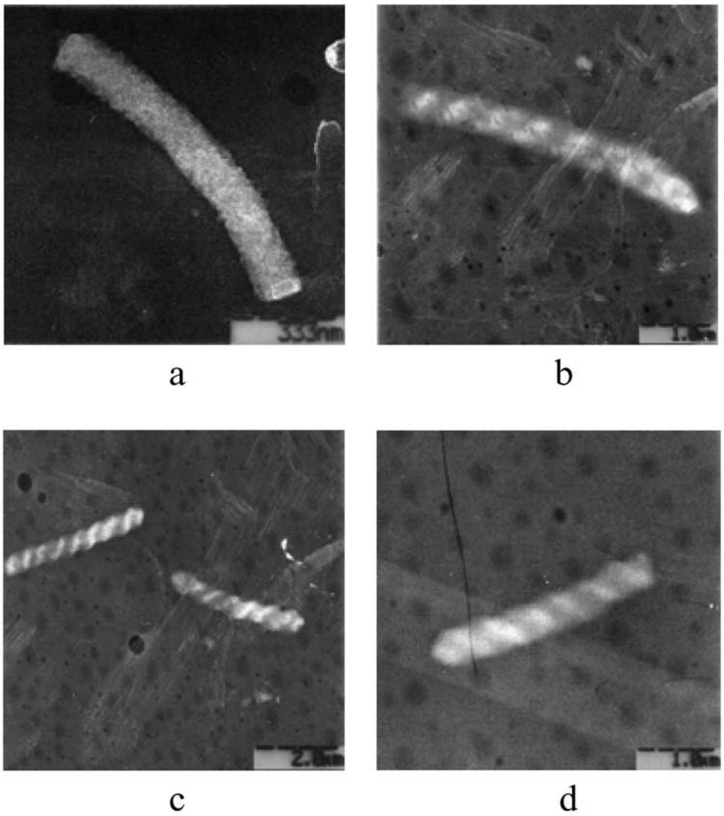

Fig. 3. TEM images of PANI–PAA synthesized under different concentration of PAA. (a) [PAA] = 0.1 mg/ml; (b) [PAA] = 0.05 mg/ml; (c) [PAA] = 0.02 mg/ml; (d) [PAA] = 0.005 mg/ml; synthetic conditions: aniline = 0.1 mol/l, aniline/APS = 1, reaction time = 14 h, temperature = 0 °C.

Again, when the concentration of PAA was higher than 0.1 mg/ml, no helical wires or rods were observed because PAA chains could not be extended in such thick solutions of high concentration and viscosity. Instead they formed large and mostly irregular aggregates that could not direct the formation of wire or rod structures. In contrast, at the PAA concentrations of lower than 0.05 mg/ml, the PAA chains should be relatively extended as microhelices at such low concentrations [35,36]. The aniline molecules attached to PAA chains by electrostatic and/or hydrogen bonding interactions to form the $(ANI)_x$/PAA adducts. Polymerization of the aniline monomers that have interactions with multiple PAA helical chains would result in the formation of large PANI–PAA assemblies. The helical structure in the microwires or rods might be induced or seeded by the helical chains of PAA. We also studied the chiral characteristic of the resulting composite microwires with CD spectra. It was found that no CD signal was observed at 465 nm, which is assigned to the absorbance of chiral polyaniline [37,38]. It indicates that the helical composite has both left-handed wire-like structure and right-handed wire-like structure, which is also proved by the TEM images in Fig. 3. Further studies are in progress to establish the mechanism of the helical wire/rod formation in this system.

3.2. Structure characterization

Fig. 4 shows FTIR spectra of PANI–PAA samples with different morphologies. There are no significant differences in the FTIR spectra when the morphology is changed. The characteristic bands of polyaniline, for example, at 3438 cm^{-1} (N–H stretching vibration), 1583 cm^{-1} (C=C stretching of the quinoid rings), 1502 cm^{-1} (C=C stretching of benzenoid rings), 1303 cm^{-1} (C–N stretching mode) and 1146 cm^{-1} (N=Q=N, where Q represents the quionoid ring) were observed in the FTIR spectra. All these bands are consistent with those reported for polyaniline prepared by conventional method [39]. Therefore, the chemical structures of PANI–PAA complexes, regardless of their morphologies, are essentially the same as each other and as conventional polyaniline. On the other hand, the characteristic bands at 1707 cm^{-1} for the PAA carbonyl C=O stretching and at 2924 cm^{-1} for the O–H stretching vibration in PAA were very weak because of the low content of PAA in the PANI–PAA complex. In order to confirm the existence of PAA in the complex, FTIR spectrum of the complex made at high PAA concentration 0.5 mg/ml was measured as given in Fig. 4(e), in which the absorption bands at 1707 and 2924 cm^{-1} are clearly identifiable. The evidence suggests that the PAA exists in the PANI wires or rods.

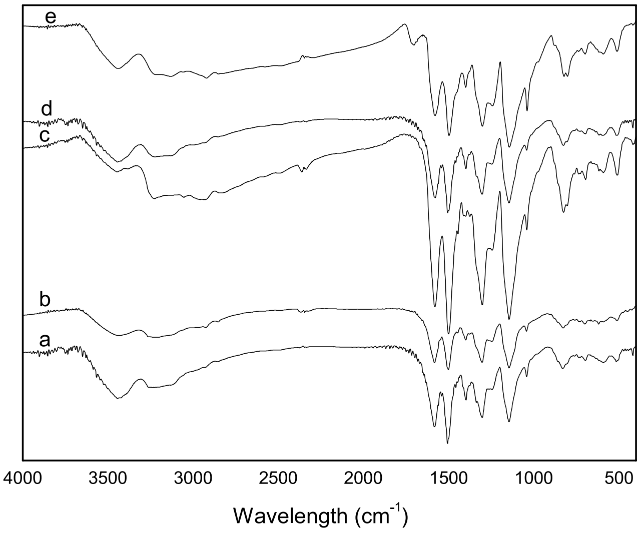

Fig. 4. FTIR spectrum of the PANI–PAA microwires synthesized under different concentration of PAA. (a) [PAA] = 0.1 mg/ml; (b) [PAA] = 0.05 mg/ml; (c) [PAA] = 0.02 mg/ml; (d) [PAA] = 0.005 mg/ml; (e) [PAA] = 0.5 mg/ml.

The UV–vis spectra of PANI–PAA wires/rods in NMP solution shows that all samples have the exciton band at 630 nm which coincide with those of neat PANI that reported earlier (Fig. 5). There was an absorption band at 320 nm due to the π–π^* transition in the benzoid ring for the samples made at the PAA concentration higher than 0.5 mg/ml (i.e. without microwire/rod formation). However, when the PAA concentration was below 0.1 mg/ml with the formation of wires/rods, two new absorption bands at 350 and 275 nm appeared. These two unexpected bands have not been reported before for doped or undoped polyaniline and it is possible that they might be related to the formation of the wire- or rod-like structures.

X-ray diffraction (XRD) patterns of PANI–PAA microwires are shown in Fig. 6. All XRD patterns are similar, and indicate the amorphous nature of the materials. These results are quite different from PANI–naphthalene sulfonic acid (NSA) microwires with high crystallinity [40]. The

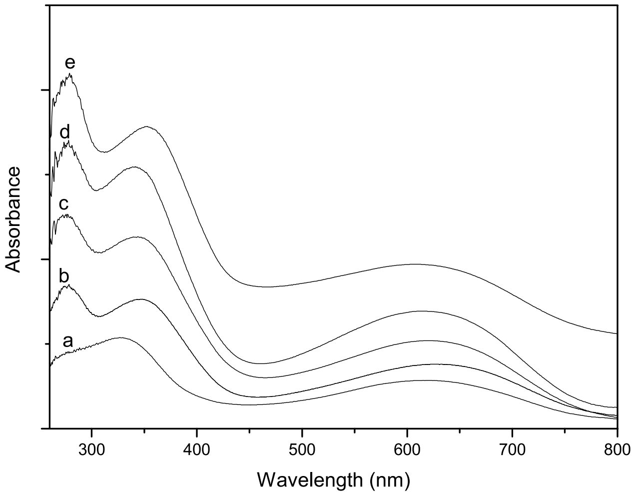

Fig. 5. UV–vis absorption spectra of the PANI–PAA microwires synthesized under different concentration of PAA. (a) [PAA] = 0.5mg/ml; (b) [PAA] = 0.1 mg/ml; (c) [PAA] = 0.05 mg/ml; (d) [PAA] = 0.02 mg/ml; (e) [PAA] = 0.005 mg/ml.

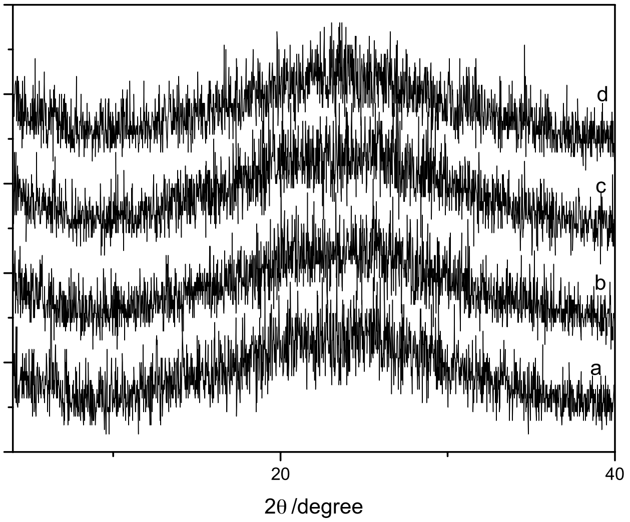

Fig. 6. XRD scattering pattern of the microwires synthesized under different concentration of PAA. (a) [PAA] = 0.1 mg/ml; (b) [PAA] = 0.05 mg/ml; (c) [PAA] = 0.02 mg/ml; (d) [PAA] = 0.005 mg/ml.

difference between PANI–PAA and PANI–NSA wires may be attributed to the difference in the wire formation mechanism. In the NSA system, the aniline monomer are protonated readily by strong acids, NSA, to form needle-like crystals of anilinium salts. As a result, the PANI–NSA microwires exhibit a high crystallinity [40]. In comparison, in the PAA system, the protonation of aniline monomer is more difficult because PAA is a weak acid and was used in low concentrations. Hence, the PANI–PAA complexes aggregated to form amorphous PANI–PAA microwires.

4. Conclusion

In summary, we have developed a new PAA-templated method to prepare polyaniline microwires or rods. At very low PAA concentrations, some of the microwires or rods were found to have helical nanostructures. Though the formation mechanism for such microwires and helical nanostructures is not yet fully understood, this work may represent a powerful and general strategy for the creation of highly structured electroactive functional nanomaterials.

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References

[1] MacDiarmid AG, Chiang JC, Richter AF. Synth Met 1987;18:285–90.
[2] Cao Y, Smith P, Heeger AJ. Synth Met 1992;48:91–7.
[3] Kang ET, Neoh KG, Tan KL. Prog Polym Sci 1998;23:277–324.
[4] Hutten PF, Hadziioannou G. In: Nalwa HS, editor. Handbook of organic conducting molecules and polymers, vol. 3. Chichester: Wiley; 1997. p. 2.
[5] Long Y, Chen Z, Wang N, Ma Y, Zhang Z, Zhang L, et al. Appl Phys Lett 2003;83:1863–5.
[6] Wu CG, Bein T. Science 1994;264:1757–9.
[7] Martin CR. Chem Mater 1996;8:1739–46.
[8] Parthasarathy RV, Martin CR. Chem Mater 1994;6:1627–32.
[9] Wang CW, Wang Z, Li MK, Li HL. Chem Phys Lett 2001;341:431–4.
[10] Michaelson JC, McEvoy AJ. Chem Commun 1994;1:79–80.
[11] Qiu HJ, Wan MX. J Polym Sci, Part A: Polym Chem 2001;39: 3485–97.
[12] Wei ZX, Zhang ZM, Wan MX. Langmuir 2002;18:917–21.
[13] Yang YS, Wan MX. J Mater Chem 2002;12:897–901.
[14] Huang LM, Wang ZB, Wang HT, Cheng XL, Mitra A, Yan YX. J Mater Chem 2002;12:388–91.
[15] Choi SJ, Park SM. Adv Mater 2000;12:1547–9.
[16] Liu JM, Yang SC. Chem Commun 1991;21:1529–31.
[17] Liu J, Lin YH, Liang L, Voigt JA, Huber DL, Tian ZR, et al. Chem Eur J 2003;9:605–11.
[18] Liang L, Liu J, Windisch CF, Exarhos GJ, Lin YH. Angew Chem, Int Ed 2002;41:3665–8.
[19] Reneker DH, Chun I. Nanotechnology 1996;7:216–23.
[20] MacDiarmid AG, Jones WE, Norns ID, Gao J, Johnson AT, Pinto NJ, et al. Synth Met 2001;119:27–30.
[21] He HX, Li CZ, Tao NJ. Appl Phys Lett 2001;78:811–3.
[22] Huang J, Virji S, Weiller BH, Kaner RB. J Am Chem Soc 2003;125: 314–5.
[23] Li W, Wang HL. J Am Chem Soc 2004;126:2278–9.
[24] Zhang X, Goux WJ, Manohar SK. J Am Chem Soc 2004;126:4502–3.
[25] Hwang JH, Yang SC. Synth Met 1989;29:E271–E6.
[26] Li S, Dong H, Cao Y. Synth Met 1989;29:E329–E36.
[27] Hu HL, Saniger JM, Bañuelos JG. Thin Solid Films 1999;347:241–7.
[28] Chen SA, Lee HT. Marcromolecules 1995;28:2858–66.
[29] Habaue S, Satonaka T, Nakano T, Okamoto Y. Polymer 2004;45: 5095–100.
[30] Agata Y, Kobayashi M, Kimura H, Takeishi M. Polymer 2002;43: 4829–33.
[31] Yuan GL, Kuramoto N. Polymer 2003;44:5501–4.
[32] Hatano T, Bae A-H, Takeuchi M, Fujita N, Kaneko K, Ihara H, et al. Angew Chem, Int Ed 2004;43:465–9.
[33] McCarthy PA, Huang JY, Yang SC, Wang HL. Langmuir 2002;18: 259–63.
[34] Li WG, McCarthy PA, Liu DG, Huang JY, Yang SH, Wang HL. Marcromolecules 2002;35:9975–82.
[35] Muroga Y, Noda I, Nagasawa MJ. Phys Chem B 1969;73:667–72.
[36] Kawaguchi Y, Nagasawa MJ. Phys Chem B 1969;73:4382–4.
[37] McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537–74.
[38] MacDiarmid AG, Norris ID, Wallace GG, Zheng W. Synth Met 1999; 106:171–6.
[39] Tang J, Jing X, Wang F. Synth Met 1988;24:231–8.
[40] Huang J, Wan MX. J Polym Sci, Part A: Polym Chem 1999;37: 1277–84.