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Chiral nanotubes of polyaniline synthesized by a template-free method

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Chiral nanotubes of polyaniline (PANI) were successfully synthesized by a template-free method in the presence of (*S*)-(−)-2-pyrrolidone-5-carboxylic acid [(*S*)-PCA)] or (*R*)-(+)-2-pyrrolidone-5-carboxylic acid [(*R*)-PCA] as the dopant for the first time. The tubular morphologies of the resulting PANI–(*S*)-PCA and PANI–(*R*)-PCA were confirmed by SEM and TEM images. The tubes are 80–220 nm in outer diameter and 50–130 nm in inner diameter. It was proposed that the micelles of aniline–(*S*)-PCA or (*R*)-PCA, which were formed due to the hydrophobic aniline and the hydrophilic -COOH group of PCA, played a "template" role during the formation of the chiral nanotubes. These chiral nanotubes showed optically active and electrical properties. In particular, a positive and a negative Cotton effect corresponding to a helical screw of the polymer main chains was observed in the chiral nanotubes. The structural characterization measured by FTIR and X-ray diffraction indicated that the configuration of PCA did not affect the main chains of the chiral nanotubes; however, short-range ordering at $2\theta = 6.43$ ($d = 13.73$ Å) was significantly observed from the chiral nanotubes, which might result from the chiral character of the dopant.

Introduction

Nowadays, nanotubes and nanowires of conducting polymers have attracted considerable attention because of their unique properties on account of their finite small size and potential applications in a variety of areas, including molecular electronics, material sciences and biomedical sciences.[1–4] The discovery of carbon nanotubes (CNTs)[5] promoted a development of nanotubes or molecular wires of conducting polymers. For example, well-defined poly (*p*-phenylenevinylene) (PPV) fibers ($d \approx 4$ nm) have been prepared within an ordered hexagonal array of hydrophilic channels produced by photo-cross-linking a polymerizable liquid crystal monomer (*e.g.* acrylate).[6] As the fibers were interspersed within the photo-cross-linked liquid crystal polymer matrices, significant fluorescence enhancement was observed. Nanowires of polypyrrole (PPy)[7] and polyaniline (PANI)[7,8] were also obtained on highly ordered pyrolytic graphite (HOPG) by scanning probe microscopy techniques. Furthermore, PPy microwires synthesized by a scanning microneedle as electrodes have been reported.[9] More generally, conjugated polymer nanofibers and nanotubes have been synthesized within the pores of a nanoporous membrane[10,11] or nanochannels of a mesoporous zeolite.[12] These so-called "template syntheses" produce monodisperse polymeric fibers or tubules with controllable diameter, length, and conductivity. However, these cases often require a rather tedious post process in order to remove the template. More recently, Wan *et. al.*[13–17] reported that micro- and nanotubes of PPy and PANI could be synthesized by a template-free method. Obviously, this method is simple and cheap compared with the "template synthesis" method because it omits the use of a nano- or microporous membrane acting as a template. However, no paper concerning chiral micro- or nanotubes of conducting polymers synthesized by a template-free method has been reported yet.

Recently, chiral conducting polymers are of considerable interest because of their potential applications such as electrodes for electrochemical asymmetric synthesis,[18,19] modified electrodes capable of performing stereoselective analysis,[20,21] novel chiral stationary phases for chromatographic separation of enantiomers,[22–24] microwave absorbents[25] and electroactive chiral membranes for selective transport enantiomer chemicals.[26] Optically active conducting polymers, such as PPy,[27–30] polythiophene (PTH)[31–33] and PANI[34–39] have been reported in the literature. However, the morphologies of these chiral conducting polymers have seldom been investigated, and only granular morphologies (200–600 nm) of chiral conducting PANI were reported.[40,41] Due to its excellent electronic and environmental stability, facile redox and pH switching between different colored states, PANI is recognized as one of the most promising organic conducting polymers. As to PANI nanotubes, it is important to functionalize them for realizing their wide range of potential applications. Therefore, it is attempted to synthesize chiral PANI nanotubes by the new template-free method.

In this article, chiral nanotubes of polyaniline were synthesized using ammonium persulfate (APS) as oxidant in the presence of (*S*)-(−)-2-pyrrolidone-5-carboxylic acid [(*S*)-PCA] or (*R*)-PCA as the dopant without involving any template. The optical activity and electrical properties of these PANI–(*R*)- or (*S*)-PCA nanotubes were investigated. In addition, the molecular structure and crystalline characterization of the chiral PANI–(*R*)- or (*S*)-PCA nanotubes were discussed.

Experimental

Materials and synthesis

Aniline was distilled and stored under $N_2(g)$ prior to use. APS as oxidant and (*R*)- or (*S*)-PCA as dopant were used without any purification. The nanotubes of PANI–(*R*)-PCA or PANI–(*S*)-PCA were synthesized by *in situ* doping polymerization in the presence of (*R*)-PCA or (*S*)-PCA as the dopant, which was called the template-free method. In a typical process, 0.73 ml of aniline monomer and 0.53 g of (*R*)- or (*S*)-PCA were mixed in 200 ml of deionized water, the

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mixture was dispersed by ultrasonic stirring at room temperature for 3 hours. Then APS was added to the above mixture, and the mixture was continuously stirred for 10 hours. Finally, the resulting precipitate was filtered and washed with deionized water, methanol, and ethyl ether several times, then dried in a dynamic vacuum at room temperature for 24 hours.

Microscopy measurements

The tubular morphology was measured by scanning electron microscopy (SEM) and further proved by transmission electron microscopy (TEM) images. These measurements were carried out on a Hitachi-530 SEM and a H-900NA TEM (300 KV) respectively. The specimens for TEM observations were prepared by crushing the PANI–(*R*)- or (*S*)-PCA samples into fine fragments and dispersing in alcohol, and then dispersing on micro-grids coated with holey carbon support film. Because the PANI–(*R*)- or (*S*)-PCA nanotubes only gave rise to a very weak contrast in TEM investigations, we enhanced it by using small objective apertures and big underfocus values.

Electrical properties

The conductivity of PANI–(*R*)- or (*S*)-PCA pellets at room temperature was measured by the standard Van Der Pauwe DC four-probe method[42] using a Keithley 196 System DMM Digital Multimeter and Advanst R1642 Programmable DC-voltage/current generator as the current source.

Spectroscopic measurements

After dissolving 1–2 milligrams of PANI–(*R*)- or (*S*)-PCA in 5 ml *m*-cresol and filtering, UV–visible spectra of the PANI–(*R*)- or (*S*)-PCA were recorded from 300 to 1200 nm using a Shimadzu UV 1601 spectrophotometer. Circular dichroism (CD) spectra (J-715 spectropolarimeter) were measured from 300 to 800 nm by dissolving about 1.5 mg PANI–(*R*)- or (*S*)-PCA in 5 ml dimethylformamide (DMF) and filtering, using a 10 mm path length cell. FTIR (Perkin-Elmer System) and X-ray diffraction (a D/max-2400) characterized the molecular structure of the PANI–(*R*)- or (*S*)-PCA.

Results and discussion

1. Morphology

The resulting chiral PANI–(*S*)-PCA synthesized by the template-free method in the presence of (*S*)-PCA as the dopant is shown in Fig. 1a. TEM images proved that these fibers are hollow. Chiral PANI–(*R*)-PCA nanotubes were also obtained when the synthesis conditions were same as those for synthesizing nanotubes of PANI–(*S*)-PCA except using (*R*)-PCA as dopant. Their typical SEM and TEM images are given in Fig. 1b. Most of the nanotubes with an outer diameter of 80–220 nm and inner diameter of 50–130 nm are hollow along the whole length and the aspect ratio of these nanotubes varies from 6 to 12. As one can see, the size of PANI–(*S*)-PCA was very close to that of PANI–(*R*)-PCA, suggesting that the different configuration of the dopants did not obviously affect the tubular morphologies of PANI–(*S*) or (*R*)-PCA.

However, it was found that the formation of these chiral nanotubes depended on the reaction conditions. For example, the concentration of aniline monomer strongly affected the morphology of the resulting PANI–(*S*)-PCA. When the concentration of aniline monomer was about 0.04 mol L^{-1}, the resulting PANI–(*S*)-PCA was tubular (see Fig. 1a); but as the

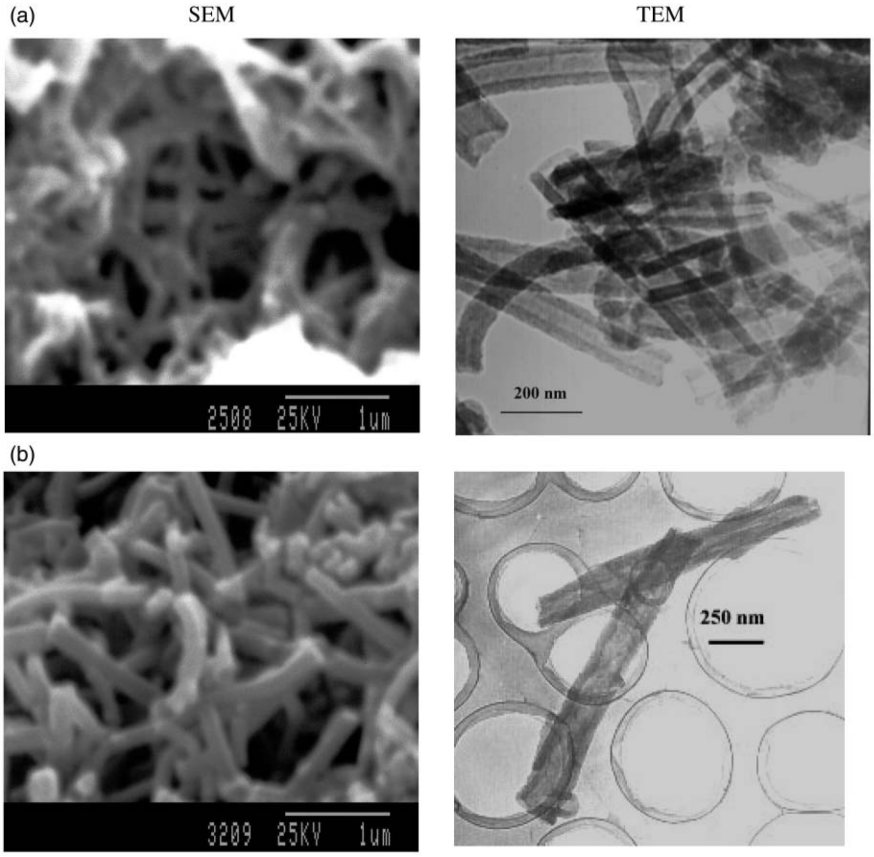

Fig. 1 SEM and TEM images of (a) PANI–(*S*)-PCA and (b) PANI–(*R*)-PCA. Synthesis conditions: [aniline] = 0.04 mol L^{-1}, [(*S*)- or (*R*)-PCA] = 0.02 mol L^{-1}, [APS]/[aniline] = 1, reaction time 10 hours, at room temperature.

concentration of aniline monomer was higher (*e.g.* 0.1 mol L^{-1} or 0.35 mol L^{-1}), only granular PANI–(*S*)-PCA was obtained. In addition, the molar ratio of aniline monomer to (*S*)-PCA could greatly change the content of these tubes in the whole product. When the molar ratio of aniline monomer to (*S*)-PCA was 2, the percentage of these fibers in the whole sample could reach 75%. If the molar ratio of aniline monomer to (*S*)-PCA was higher or lower than 2, the content of these tubes in both cases was decreased. When the molar ratio of that was lower than 0.25 or higher than 4, almost no tube was observed.

Based on our previous results,[43,44] it is expected that the micelles of the aniline monomer–(*R*)-PCA or (*S*)-PCA formed due to the hydrophobic aniline and the hydrophilic -COOH group of (*R*)- or (*S*)-PCA played a template role during the process, forming chiral PANI–(*R*) or (*S*)-PCA tubes.

2. Optical activity

Fig. 2 shows the CD spectra of PANI–(*S*)-PCA and PANI–(*R*)-PCA nanotubes dissolved in DMF. Significantly, the distinctive bands of spectra for PANI–(*S*)- or (*R*)-PCA nanotubes at 331 nm and 380 nm were observed, which may be assigned as the exciton-coupled bands associated with the PANI absorption band at *ca.* 400 nm.[41] The positive and negative Cotton effect indicates a helical sense of the polymer main chains of PANI–(*S*)- or (*R*)-PCA tubes.[45] Because the concentration of (*S*)- or (*R*)-PCA was no more than 9.5 × 10^{-4} mol L^{-1} under measuring conditions, it was impossible that the absorption of (*S*)- or (*R*)-PCA could be detected. Therefore, the Cotton effects only were caused by the macromolecular asymmetry of PANI–(*S*)- or (*R*)-PCA nanotubes. In contrast, the DMF solutions of PANI–(*S*)- or (*R*)-PCA nanotubes produced mirror-image CD spectra. This suggests that the protonation of PANI is enantioselective, with one or other helical screw of the polymer chains, depending on which hand of the PCA is incorporated.[46] Comparing the CD spectra of PANI–(*S*)- or (*R*)-PCA nanotubes with those of PANI doped with (*R*)- or (*S*)-camphorsulfonic acid (CSA),[46] the peaks of the former were shifted from 450 and 390 nm to 380 and 330 nm. Furthermore, there is no obvious band near 800 and 700 nm in PANI–(*S*)- or (*R*)-PCA. These may be related to the different geometries of their chiral counter anions and the conformation of their polymer chains.

3. Electrical properties

The room-temperature conductivity of PANI–(*S*)-PCA increased with increasing the molar ratio of (*S*)-PCA to aniline monomer as shown in Fig. 3. This may be ascribed to the higher doping level of the PANI main chains relating to the higher concentration of (*S*)-PCA. The room-temperature conductivity of PANI–(*S*)-PCA nanotubes (*ca.* 8.3 × 10^{-6} S cm^{-1}) is almost identical with that of PANI–(*R*)-PCA nanotubes (*ca.* 4.0 × 10^{-6} S cm^{-1}). When the concentration of aniline monomer is higher (*e.g.* 0.35 mol L^{-1}), and there is a higher molar ratio of (*S*)-PCA to aniline (*e.g.* 4), however, only granular PANI–(*S*)-PCA was obtained; the room-temperature conductivity of the granular PANI–(*S*)-PCA can reach 0.40 S cm^{-1}. This value is close to that of PANI doped by other sulfonic acids.[14] The poor conductivity of the tubes may result from a low doping level.

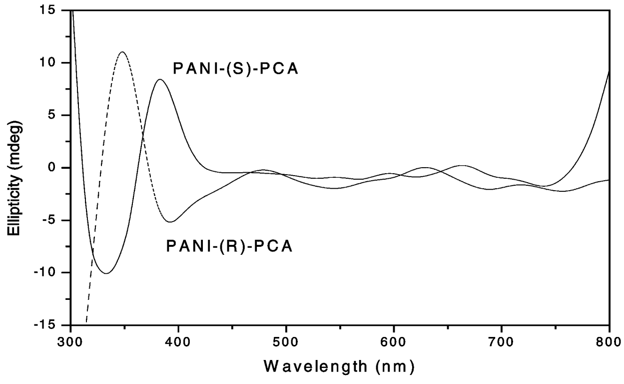

Fig. 2 CD spectra of the chiral tubes of (a) PANI–(*S*)-PCA and (b) PANI–(*R*)-PCA. Reaction conditions: [aniline] = 0.04 mol L^{-1}, [(*S*)- or (*R*)-PCA] = 0.02 mol L^{-1}, [APS] /[aniline] = 1, reaction time 10 hours, at room temperature.

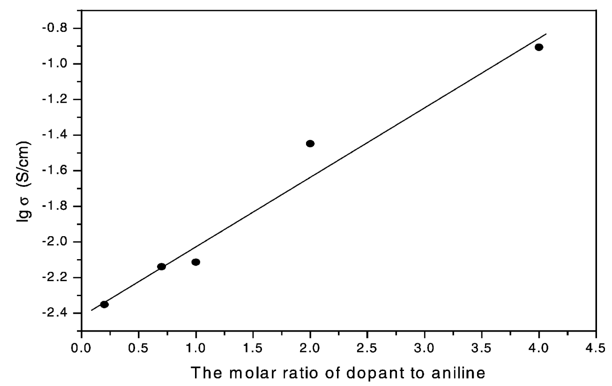

Fig. 3 The effect of the molar ratio of (*S*)-PCA to aniline monomer on the room-temperature conductivity of resulting PANI–(*S*)-PCA. Reaction conditions: [aniline] = 0.10 mol L^{-1}, [APS]/[aniline] = 1, reaction time 10 hours, at room temperature.

4. Structure characterization

As Fig. 4 shows, the UV–visible spectra of PANI–(*S*)- or (*R*)-PCA nanotubes with low conductivity (~10^{-6} S cm^{-1}) only present one strong peak at 400 nm, which assigned as a second polaron band.[47] Moreover, there is not much difference in UV–visible spectra between PANI–(*S*)-PCA and PANI–(*R*)-PCA nanotubes. For the granular PANI–(*S*)- or (*R*)-PCA with high conductivity (0.4 S cm^{-1}), however, the second polaron band shifted to 440 nm and a polaron band at 960 nm with free tail were observed. Thus, the difference described above in the UV–visible spectra might be the reason that the conductivity of the tubes is lower than that of grains.

FTIR spectra of PANI–(*S*)- or (*R*)-PCA tubes are given in Fig. 5. The characteristic bands of the emeraldine salt of PANI, for example, the C=C stretching of quinoid and benzenoid

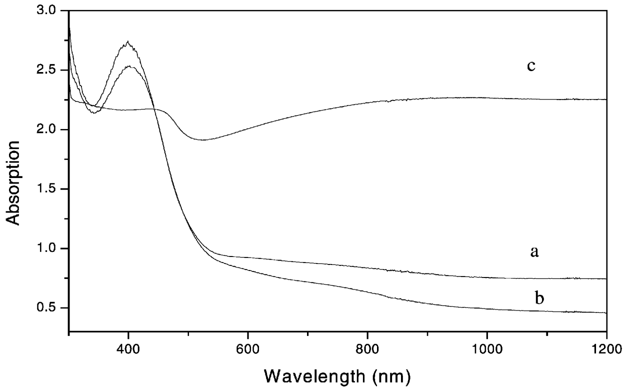

Fig. 4 UV–visible absorption spectra of the chiral nanotubes and grains dissolved in *m*-cresol. (a) PANI–(*S*)-PCA nanotubes, (b) PANI–(*R*)-PCA nanotubes, [aniline] = 0.04 mol L^{-1}, [(*S*)- or (*R*)-PCA] = 0.02 mol L^{-1}; (c) granular PANI–(*S*)-PCA, [aniline] = 0.35 mol L^{-1}, [(*S*)-PCA] = 1.40 mol L^{-1}. Other reaction conditions: [APS]/[aniline] = 1, reaction time 10 hours, at room temperature.

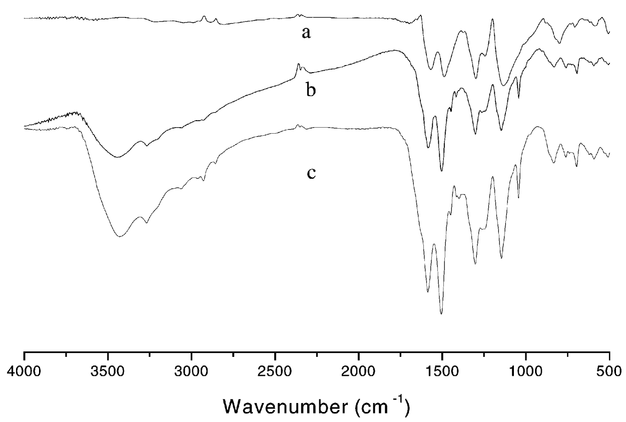

Fig. 5 FTIR spectra of the chiral nanotubes and grains. (a) granular PANI–(*S*)-PCA, [aniline] = 0.35 mol L^{-1}, [(*S*)-PCA] = 1.40 mol L^{-1}; (b) PANI–(*S*)-PCA nanotubes, (c) PANI–(*R*)-PCA nanotubes, [aniline] = 0.04 mol L^{-1}, [(*S*)- or (*R*)-PCA] = 0.02 mol L^{-1}. Other reaction conditions: [APS]/[aniline] = 1, reaction time 10 hours, at room temperature.

rings bands centered at 1567 and 1487 cm^{-1}, the C–N stretching mode at *ca.*1300 cm^{-1}, the absorption peaks of N=Q=N (Q representing the quinoid ring) at *ca.* 1140 cm^{-1}, and the N–H stretching vibration at 3400 cm^{-1}[48] were observed. However, the peaks of the chiral PANI–(*S*)- or (*R*)-PCA nanotubes corresponding to the C=C stretching of quinoid and benzenoid rings were blue shifted to 1595 and 1504 cm^{-1}, compared with that of PANI–NSA microtubes.[14] This may result from the shorter conjugation length of their polymer main chains. Perhaps related to their different condensed states, the peak of granular PANI–(*S*)-PCA with higher conductivity (0.40 S cm^{-1}) corresponding to the N–H stretching vibration at 3400 cm^{-1} is much weaker than that of the chiral nanotubes. It is noted that the characteristic band of the granular PANI–(*S*)-PCA sample at 1700 cm^{-1} assigned as the carbonyl group[49] stretching vibration can be easily observed. This evidence directly proves that the PANI is doped by (*S*)-PCA. As to the chiral PANI–(*S*)- or (*R*)-PCA nanotubes, the content of the carbonyl group is so low that this peak can not be observed.

X-Ray scattering patterns of PANI–(*S*)- or (*R*)-PCA nanotubes are shown in Fig. 6. For chiral nanotubes of PANI–(*S*)- or (*R*)-PCA, a sharp peak at $2\theta = 6.43$ and two other broad bands centered at $2\theta = 18.35$ and 25.93 could be observed. But, only broad peaks centered at $2\theta = 20.78$ and 25.40 appeared in the X-ray scattering patterns of granular PANI–(*S*)- or (*R*)-PCA. The sharp peak at $2\theta = 6.43$ ($d = 13.73$ Å) was assigned as the periodicity distance between the dopant and N atom on adjacent main chains.[44] Thus, the sharp peak at $2\theta = 6.43$ observed in the chiral tubes indicates a short range ordering between the chiral counter anion and the polymer chain, which might related to the tubular morphologies of PANI–(*S*)-PCA or PANI–(*R*)-PCA. This is consistent with the fact that this sharp peak is absent for the granular PANI–(*S*)-PCA or PANI–(*R*)-PCA.

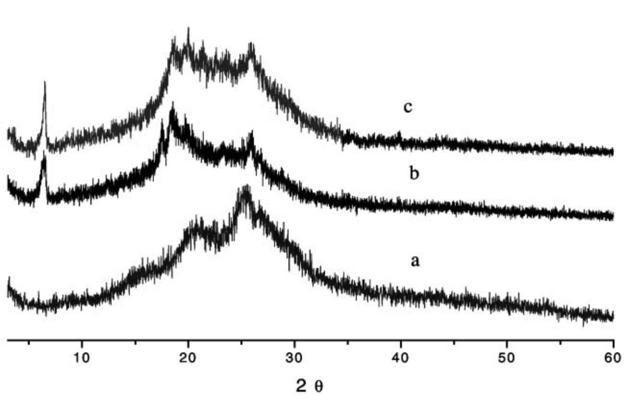

Fig. 6 XRD scattering pattern of the chiral nanotubes and grains. (a) granular PANI–(*S*)-PCA, [aniline] = 0.35 mol L^{-1}, [(*S*)-PCA] = 1.40 mol L^{-1}; (b) PANI–(*S*)-PCA nanotubes, (c) PANI–(*R*)-PCA nanotubes, [aniline] = 0.04 mol L^{-1}, [(*S*)- or (*R*)-PCA] = 0.02 mol L^{-1}. Other reaction conditions: [APS]/[aniline] = 1, reaction time 10 hours, at room temperature.

Conclusion

1. Chiral nanotubes of PANI–(*S*)-PCA or PANI–(*R*)-PCA were firstly synthesized by a template-free method in the presence of (*S*)- or (*R*)-PCA as the dopant; they are 80–220 nm in outer diameter and 50–130 nm in inner diameter. Most of these chiral nanotubes with aspect ratios of 6–10 are hollow along the whole length. A chemical yield of 75% nanotubes can be achieved when the concentration of aniline monomer is about 0.04 mol L^{-1} and the molar ratio of aniline to (*S*)- or (*R*)-PCA is 2.

2. The chiral PANI–(*S*)- or (*R*)-PCA nanotubes were optically active. The positive and negative Cotton effect observed in these PANI–(*S*)- or (*R*)-PCA nanotubes revealed a helical screw of the polymer main chains. The observed mirror-imaged circular dichroism spectra for these nanotubes indicated an enantioselectivity during *in situ* doping polymerization depending on which hand of the chiral PCA was incorporated. The room temperature conductivity of the chiral nanotubes is about 10^{-6} S cm^{-1}.

3. Structure characterization by FTIR and X-ray diffraction indicated that the main chains of the PANI–(*S*)-PCA nanotubes are identical to those of the PANI–(*R*)-PCA tubes and both are partially crystalline.

4. It was proposed that the micelles of aniline–(*S*)- or (*R*)-PCA formed due to hydrophobic aniline and the hydrophilic -COOH group of PCA played a template role in forming chiral nanotubes.

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References

1 Z. Yao, H. W. C. Postma, L. Balents and C. Dekker, *Nature*, 1999, **402**, 273.
2 D. Normile, *Science*, 1999, **286**, 2056.
3 J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dai, *Science*, 2000, **287**, 622.
4 R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. D. Rossi, A. G. Rinzer, O. Jaschinski, S. Roth and M. Kertes, *Science*, 1999, **284**, 1340.
5 (*a*) S. Iijma, *Nature*, 1991, **354**, 56; (*b*) Recent reviews, for example: M. Terrones, W. K. Hsu, J. P. Hare, H. W. Kroto, H. Terrones and D. R. M. Walta, *Philos. Trans. R. Soc. London A*, 1996, **354**, 2025; (*c*) B. I. Yakobson and R. E. Smalley, *Am. Sci.*, 1997, **85**, 325; (*d*) P. M. Ajayan and T. W. Ebbesen, *Rep. Prog. Phys.*, 1997, **60**, 1026; (*e*) L. Dai, *Polym. Adv. Technol.*, 1999, **10**, 357; (*f*) L. Dai and A. W. H. Mau, *J. Phys. Chem. B*, 2000, **104**, 1891.
6 R. C. Smith, W. M. Fischer and D. L. Gin, *J. Am. Chem. Soc.*, 1997, **119**, 4092.
7 X. W. Cai, J. S. Gao, Z. X. Xie, Y. Z. Xie, Q. Tian and B. W. Mao, *Langmuir*, 1998, **14**, 2508.
8 M. N. Ralph and M. P. Reginald, *J. Phys. Chem.*, 1996, **100**, 17041.
9 S. Shirators, S. Moriand and K. Ikeyaki, *Sens. Actuators, B.*, 1998, **49**, 30.
10 (*a*) C. R. Martin, *Acc. Chem. Res.*, 1995, **259**, 957; (*b*) R. Jérôme, *Chem. Eur. J.*, 2000, **6**, 3089.

11 (*a*) Z. Cai, J. W. Lei, V. M. Liang and C. R. Martin, *Chem. Mater.*, 1991, **3**, 960; (*b*) C. R. Martin, *Science*, 1994, **266**, 1961; (*c*) C. R. Martin, *Chem. Mater.*, 1996, **8**, 1739; (*d*) J. C. Hulteen and C. R. Martin, *J. Mater. Chem.*, 1997, **7**, 1075; (*e*) X. M. Cepak and C. R. Martin, *Chem. Mater.*, 1999, **11**, 1363; (*f*) Z. Cai and C. R. Martin, *J. Am. Chem. Soc.*, 1989, **111**, 4138; (*g*) R. V. Parthsarathy and C. R. Martin, *Chem. Mater.*, 1994, **6**, 1627; (*h*) V. Mennen, *Synth. Met.*, 1993, **55**, 1165.

12 C. G. Wu and T. Bein, *Science*, 1994, **264**, 1759.

13 M. Wan, Y. Shen and J. Huang, Chinese Patent No. 981099165, 1998.

14 J. Huang and M. Wan, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 1277.

15 Y. Shen and M. Wan, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 1443.

16 M. Wan and J. Li, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 4605.

17 (*a*) M. Wan, J. Huang and Y. Shen, *Synth. Met.*, 1999, **101**, 708; (*b*) H. Qiu, M. Wan, B. Matthews and L. Dai, *Macromolecules*, 2001, **34**, 675.

18 M Schwientek, S. Plens and C. H. Hamann, *J. Electroanal. Chem.*, 1999, **461**, 94.

19 S. Pleus and M. Schwientek, *Synth. Met.*, 1998, **95**, 233.

20 Z. D. Chen, Y. Takei, B. A. DeoYe and T. Nagaoka, *Analyst*, 2000, **125**, 2249.

21 (*a*) L. Mare, D. Diadier, G. Robert, G. Alain and R. Jean, *J. Chem. Soc., Chem. Commun.*, 1988, 658; (*b*) Y. X. Zhou, B. Yu and G. Y. Zhu, *Polymer*, 1997, **38**, 5493.

22 H. S. Lee and J. Hong, *J. Chromatogr. A.*, 2000, **868**, 189.

23 Z. D. Chen, A. Okimoto, T. Kiyonaga and T. Nagaoka, *Anal. Chem.*, 1999, **71**, 1834.

24 H. L. Guo, C. M. nobler and R. B. Kaner, *Synth. Met.*, 1999, **101**, 44.

25 G. C. Sun, K. L. Yao, H. X. Liao, Z. C. Niu and Z. L. Liu, *Int. J. Electron.*, 2000, **87**, 735.

26 L. A. P. Kane-Maguire, I. D. Norris and G. G. Wallace, *Synth. Met.*, 1999, **101**, 817.

27 D. Delabouglise and F. Garnier, *Synth. Met.*, 1990, **39**, 117.

28 M. Salmon, M. Saloma, G. Bidan and E. M. Genies, *Electrochim. Acta*, 1989, **34**, 117.

29 J. C. Moutet, E. Saint-Aman, F. Tran-Van, P. Angibeaud and J. P. Utille, *Adv. Mater.*, 1992, **4**, 511.

30 (*a*) R. L. Elsenbaumer, H. Eckhardt, Z. Iqbal, J. Toth and R. H. Baughman, *Mol. Cryst. Liq. Cryst.*, 1988, 917; (*b*) F. Chen, P. Akhtar, L. A. P. Kane-Maguire and G. G. Wallace, *Aust. J. Chem.*, 1997, **50**, 939.

31 D. Kotkar, V. Joshi and P. K. Ghosh, *J. Chem. Soc., Chem. Commun.*, 1988, 917.

32 (*a*) M. Lemaire, D. Delabouglise, R. Garreau, A. Gay and J. Roncal, *J. Chem. Soc., Chem. Commun.*, 1988, 658; (*b*) M. Lemaire, D. Delabouglise, R. Garreau and J. Roncal, *Chim. Phys.-Chim. Biol.*, 1989, **86**, 193.

33 M. Anderson, P. O. Ekeblad, T. Hjertberg, O. Wennerström and O. Inganäs, *Polymer*, 1991, **32**, 546.

34 S. A. Asharf, L. A. P. Kane-Maguire, M. R. Majidi, S. G. Pyne and G. G. Wallace, *Polymer*, 1997, **38**, 2627.

35 M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Aust. J. Chem.*, 1998, **51**, 23.

36 E. V. Strounina, L. A. P. Kane-Maguire and G. G. Wallace, *Synth. Met.*, 1999, **106**, 129.

37 I. D. Norris, L. A. P. Kane-Maguire, G. G. Wallace and L. H. C. Mattoso, *Aust. J. Chem.*, 2000, **153**, 89.

38 J. V. Barris, P. C. Innis, L. A. P. Kane-Maguire, I. D. Norris and G. G. Wallace, *Synth. Met.*, 1997, **84**, 181.

39 M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Polymer*, 1996, **37**, 359.

40 V. Aboutanos, J. N. Barisci, L. A. P. Kane-Maguire and G. G. Wallace, *Synth. Met.*, 1999, **106**, 89.

41 P. C. Innis, I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, *Macromolecules*, 1998, **31**, 6521.

42 V. Pauwe and L. T. Philips, *Res. Rep.*, 1958, **13**, 1.

43 J. Liu and M. Wan, *J. Mater. Chem.*, 2001, **11**, 404.

44 M. Wan and J. Li, *J. Polym. Sci. Part A: Polym. Chem.*, 2000, **38**, 2359.

45 K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa and M. Kyotani, *Science*, 1998, **27**, 282.

46 M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, *Poymer*, 1995, **36**, 3597.

47 Y. Xia, J. M. Wiesinger, A. G. MacDiarmid and A. J. Epstein, *Chem. Mater.*, 1995, **7**, 443.

48 J. Tang, X. Jing and F. Wang, *Synth. Met.*, 1988, **24**, 231.

49 L. Chierici and G. P. Gardini, *Tetrahedron*, 1966, **22**, 53.