

Large induced optical activity in the conduction band of polyaniline doped with (1S)-(+)-10-camphorsulfonic acid

Citation for published version (APA):

Havinga, E. E., Bouman, M. M., Meijer, E. W., Pomp, A., & Simenon, M. M. J. (1994). Large induced optical activity in the conduction band of polyaniline doped with (1S)-(+)-10-camphorsulfonic acid. *Synthetic Metals*, 66(1), 93-97. DOI: 10.1016/0379-6779(94)90168-6

DOI:

[10.1016/0379-6779\(94\)90168-6](https://doi.org/10.1016/0379-6779(94)90168-6)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Short communication

Large induced optical activity in the conduction band of polyaniline doped with (1*S*)-(+)–10-camphorsulfonic acid

E.E. Havinga^{a,b}, M.M. Bouman^b, E.W. Meijer^b, A. Pomp^a, M.M.J. Simenon^a

^aPhilips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, Netherlands

^bLaboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

Received 12 May 1994; accepted 13 May 1994

Abstract

A large induced circular dichroism is found in the conduction band of polyaniline doped with optically active camphorsulfonic acid. In films obtained by spin-coating from a *meta*-cresol solution, the chiral dopant induces chirality within the main chain of polyaniline. No other combinations of achiral conducting polymers and chiral dopants have been found that show induced optical activity in their conduction band.

Keywords: Polyaniline; Optical activity; Camphorsulfonic acid

1. Introduction

Optical activity in the π – π^* absorption band of conjugated polymers can be induced by the presence of chirality in the side chains. Examples have been reported for polythiophenes [1–7], polypyrroles [1,8,9], polyacetylenes [10–13], poly(phenylene-vinylene)s [14,15] and poly(diacetylene)s [16] substituted with optically active side chains. Regioregularity in the side-chain substitution pattern is of importance to obtain very large circular dichroism (CD) effects [6,7]. It is argued that this induced chirality is only present if the polymers are either in the solid state or in an agglomerated or associated phase in a poor solvent [6,7]. Induced chirality is absent in solutions of a good solvent, as is shown for polythiophenes [2,6,7]. Furthermore, most induced CD spectra show a marked exciton splitting [2,6,7,9,16]. The axial chirality in these inherently dissymmetric systems is ascribed to a helical shape of the conjugated main chain in the 'solid' state, which is induced by the optically active side chains. The two helices possible for the main chains have a diastereomeric relationship. Due to the marginal difference in energy for both helices, cooperative interchain interactions and a crystalline-like state are required to favour one helical form over the other. Only packing arguments can explain the large influence of the rel-

atively simple stereocentres that are, moreover, well separated from the main chain.

In doped samples of these conjugated polymers the induced chirality is smaller. In some cases of polypyrroles [8,9] and polythiophenes [2–5], however, appreciable induced chirality is present. Moreover, a significant selectivity as to doping with different enantiomers of chiral dopant ions is found for chiral polythiophenes, substituted with optically active side chains [3,4].

With this selectivity for chiral dopants on chiral polymers in mind, we have investigated the possibility of inducing chirality in the conduction band of a conjugated polymer, in itself achiral, solely due to the presence of a chiral dopant. This concept presupposes, of course, that the chiral dopant ions arrange themselves in regular stacks on the conjugated chains by electrostatic interactions, and in this way can give rise to a geometry very similar to that formed by the chirality of the side chains in the cases described above. If the dopant ions, on the contrary, occupy more randomly distributed positions, little or no CD is expected. It may be remarked that a number of conjugated polymers doped with chiral dopants have been reported, however, without any investigation whether or not this kind of doping induces chirality in the main chain [17]. A racemic mixture of chiral ions has been used in polyaniline–camphorsulfonic acid films, reported to possess superior properties with respect to conductivity [18,19]. This prompted us to investigate this system with camphorsulfonic acid as

the first choice. In fact, it turned out to be the only system in which the proposed concept of chirality in the conjugated main chain induced merely by doping with a chiral dopant worked out well.

2. Experimental

UV–Vis absorption spectra were measured with a Perkin-Elmer Lambda 3B spectrometer. CD spectra were recorded with a Jasco J600 spectropolarimeter. Conductivities (σ) were measured with the four-probe method. Aniline and pyrrole (Aldrich) were distilled under nitrogen before use; (1*S*)-(+)-10-camphorsulfonic acid ((+)-CSA, **1**, Aldrich), 3,4-(ethylenedioxy)thiophene (EDOT), (1*S*)-(+)-3-bromocamphor-10-sulfonic acid (**2**), and the chiral phosphoric acids (**3a–c**, Syncom by, Groningen, The Netherlands) were used as received (Scheme 1). The ferric salt of (+)-CSA was obtained by treatment with colloidal ferric hydroxide (H. van Hal of Philips Research). The inorganic salts and organic solvents were used as received (Aldrich, Janssen).

Polyaniline/(+)-CSA films were prepared according to the literature procedures for polyaniline/(\pm)-CSA [18,19]. Polyaniline (PANI) was synthesized by oxidative coupling of aniline with ammonium persulfate in an aqueous HCl solution at 0 °C, using a reaction time of 5 h. The resulting PANI/HCl was washed with deionized water until a pH of 6–7, dried in vacuo for 48 h, de-doped by ammonia (3% solution), washed with deionized water until pH 7–8, washed with methanol to remove oligomers, washed with diethyl ether to remove traces of methanol and water and dried again. Part of the resulting PANI base (0.3 g) was dispersed in *meta*-cresol (25 g) using an ultrasonic needle (5 min), a solution of the (+)-camphorsulfonic acid (molar ratio to repeat unit of PANI 1:2) in chloroform (5 g) added and treated again by the ultrasonic needle for 6 min. The mixture was centrifuged for 10 min at 12 500 rpm, and the decanted solution was spin-coated (first at 300 rpm for 3–5 s, followed by 750–2000 rpm during 25 s)

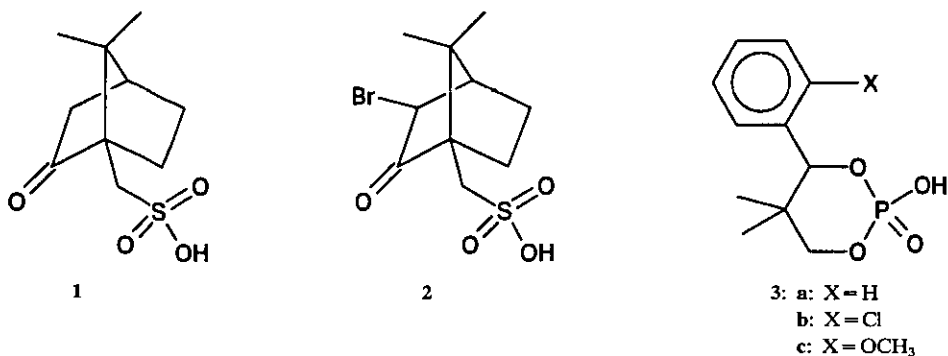
on either glass or PMMA platelets. The samples were dried at 110 °C for 30 min.

Samples of poly(3,4-(ethylenedioxy)thiophene) (PEDOT) doped with (+)-CSA were prepared by dissolving the ferric salt of (+)-CSA and the monomer EDOT in methanol (molar ratio 2.5:1), spin-coating at 300 and 1000 rpm on glass or PMMA plates, respectively, heating on a hot plate to 100 °C for 10 min and washing out the salts using deionized water. Samples of polypyrrole (PPy) doped with (+)-CSA were prepared by electrochemical polymerization of pyrrole on ITO (indium–tin-oxide)-coated glass plates from a solution of pyrrole and (+)-CSA in acetonitrile at 1.2 V(SCE) for 5 min.

3. Results and discussion

We have prepared and characterized several systems of achiral PANI doped with various enantiomerically pure ions, namely (1*S*)-(+)-10-camphorsulfonic acid ((+)-CSA, **1**), (1*S*)-(+)-3-bromocamphor-10-sulfonic acid (**2**), and three different phosphoric acids **3a–c** (Scheme 1). Moreover, we have investigated two other polymers doped with (+)-CSA (**1**), namely, PPy and PEDOT. Thin films of the polymer/chiral dopant systems have been prepared by spin-coating on either glass or PMMA, except for PPy/(+)-CSA, which was grown electrochemically on ITO-coated glass plates.

For all polymer/chiral/dopant combinations the UV–Vis absorption spectra are similar to spectra published for the corresponding heavily doped conducting polymers. Moreover, the conductivities are in agreement with data published for similar polymers. In all but one system, however, no trace of induced chirality in the polymer backbone has been detected; CD spectra show no trace of a Cotton effect in the conduction band of the conjugated polymer. The only system in which the concept of main chain chirality induced by optically active dopant worked out satisfactorily is the combination of polyaniline/(+)-camphorsulfonic acid (PANI/(+)-CSA) film, spin-coated from a *meta*-cresol solution [18,19].



Scheme 1.

The Vis absorption and the corresponding CD spectra of the PANI/(+)-CSA film on a PMMA substrate are given in Fig. 1. From these spectra it is seen that in the NIR band, generally ascribed to the transition between bands of the charge carriers ('bipolaron band'), a marked Cotton effect is present. The maximum circular anisotropy factor (g value) varies with the preparation conditions of the layers between 0.04 and 0.07, which is exceptionally high for a strongly allowed absorption band and even higher than the values of about 0.02 found for the undoped regioregular polythiophenes with induced chirality due to the chiral side chains [6,7]. The wavelength restrictions in our CD instrument do not allow us to verify whether or not the CD band has an exciton splitting. However, partially de-doping the sample (by treatment with diluted ammonia, leading to a decrease of the specific conductivity, σ , from 300 to 0.01 S/cm) shifts the absorption band to lower wavelengths and then the CD band shows clearly the expected exciton splitting (Fig. 2). Samples de-doped to even much lower conductivities show a similar CD band. Corresponding experiments with the PANI/(+)-CSA layers spun on glass substrates ($\sigma = 100$ S/cm) give identical absorption curves and isomorphous CD curves, but the magnitude of the Cotton effect is smaller by a factor of about two. This indicates again that the magnitude of the CD effect is very sensitive to variations in preparation conditions. Therefore, it is a valuable tool to probe the quality of the films prepared. CD spectra of the PANI/(+)-CSA solution in *meta*-cresol show no Cotton effect at all. This substantiates the condition that some kind of solid state order is needed to induce chirality in π -conjugated chains.

From the results on the PANI/(+)-CSA system it is clear that the induction of chirality in the conjugated main chain, merely by doping with an optically active

dopant ion, can be performed very effectively. All the chiral ions used in this study are the conjugated bases of well-known acids used in the resolution of racemic amines by the crystallization of diastereomeric salts. Camphorsulfonic acid, for instance, is commercially used to obtain an enantioselective crystallization of derivatives of racemic phenylglycine [20]. From the failure to observe any CD effect in the systems other than PANI/(+)-CSA, we are prompted to conclude that a perfect fit in the case of polymeric salts is required; the coordination of the main chain by dopant ions via electrostatic attraction only is, apparently, not sufficient to arrive at the ordered coordination needed for induced chirality in these polymers. A possible reason for the additional order in the PANI/(+)-CSA films could be that, besides the ionic interaction between the sulfonate group and a $-\text{NH}^+$ group, a hydrogen bond between a neighbouring $-\text{NH}-$ group and the ketone functionality of the CSA is not unlikely. This would lead to a more regular coordination and, in the case of optically active CSA, to induced one handedness in chirality. The exciton coupling observed in the CD points to a Davydov splitting in the conduction band. However, a detailed discussion on the supramolecular arrangement of the PANI/CSA based on this exciton splitting is far too speculative. Therefore, we restrict ourselves to the proposal that PANI/CSA is packed in some kind of a helical arrangement, e.g., such as sketched in Fig. 3.

For films made from the PANI/CSA/*meta*-cresol combination unique and superior properties as to conductivity and stability have been reported [18,19]. The extremely large Cotton effect in the CD spectra, presented above for this combination when a single enantiomer of the dopant is used, shows that a highly ordered state is present and illustrates the importance

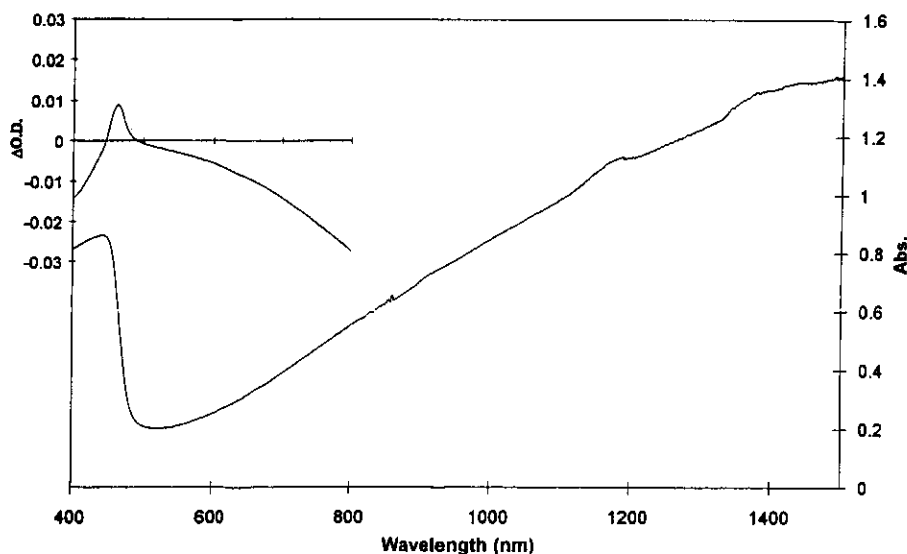


Fig. 1. Vis absorption and CD spectra of PANI/(+)-CSA on PMMA.

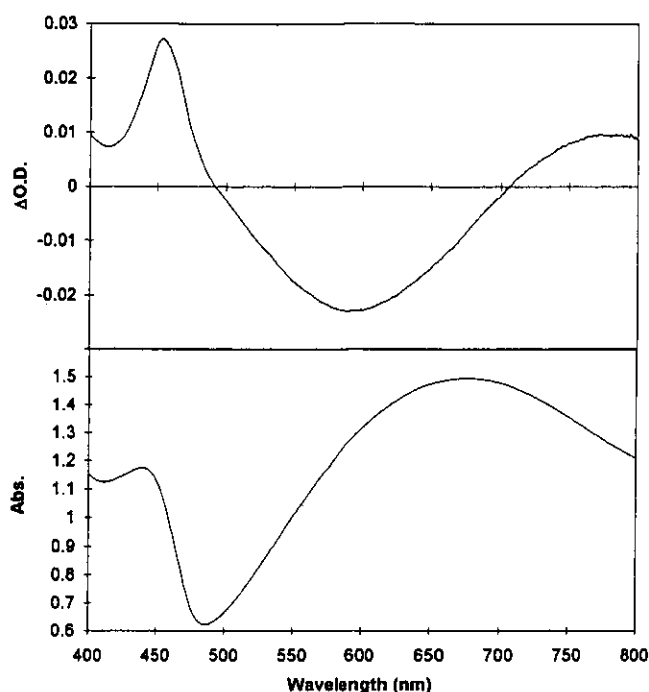


Fig. 2. Vis absorption and CD spectra of PANI/(+)-CSA on PMMA, but partially de-doped by treatment with diluted ammonia.

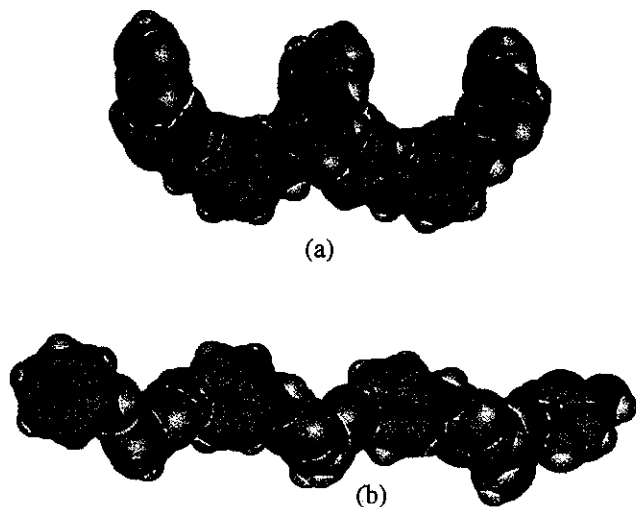


Fig. 3. Two possible helical structures of PANI: (a) *cisoid*; (b) *transoid* conformation.

of order for conducting polymers. By using a racemic mixture of (\pm)-CSA it is, obviously, not possible to measure any induced chirality by CD spectroscopy. However, the same chiral ordering will be present on a microscopic scale if the system gives rise to a phase separation in domains of ordered right- and left-handed PANI/CSA. Otherwise, no special regularity in the case of racemic CSA can be expected. Recently, we are informed that the same superior properties as to conductivity and stability are found in racemic as well as

in optically active systems [21]. A phase separation in diastereomeric domains, a phenomenon often observed in the resolution of amines with CSA, is in accordance with these observations.

4. Conclusions

We have observed a very large induced CD in the Vis-NIR absorption band in layers of PANI doped with optically active camphorsulfonic acid. The induction of chirality in the backbone of the conjugated conductive polymer is brought about by forming some kind of helix via ordered packing of the dopant along the chains, possibly by virtue of a secondary hydrogen-bridged bond. Combinations of conductive polymers and dopants that cannot form such additional bonds are not capable of inducing this CD effect. The mere observation of this large Cotton effect in the PANI/(+)-CSA system proves beyond doubt that this combination of dopant and conjugated polymer forms a very regularly ordered structure. Moreover, we have shown that CD spectroscopy is an excellent tool to probe structural order, due to the sensitivity of the Cotton effect for sample preparation.

References

- [1] D. Kotkar, V. Joshi and P.K. Ghosh, *J. Chem. Soc., Chem. Commun.*, (1988) 917.
- [2] M. Andersson, P.O. Ekeblad, T. Hjetberg, O. Wennerström and O. Ingenäs, *Polym. Commun.*, 32 (1991) 546.
- [3] M. Lemaire, D. Delabouglise, R. Garreau and J. Roncali, in S. Torii (ed.), *Recent Advances in Electroorganic Synthesis*, Kodansha Ltd., Tokyo, 1987, p. 385.
- [4] M. Lemaire, D. Delabouglise, R. Garreau, A. Guy and J. Roncali, *J. Chem. Soc., Chem. Commun.*, (1988) 658.
- [5] J. Roncali, R. Garreau, D. Delabouglise, F. Garnier and M. Lemaire, *Synth. Met.*, 28 (1989) C341.
- [6] M.M. Bouman and E.W. Meijer, *Polym. Prepr.*, 35 (1994) 309.
- [7] M.M. Bouman, E.E. Havinga, R.A.J. Janssen and E.W. Meijer, *Mol. Cryst. Liq. Cryst.*, in press.
- [8] M. Salmon, M. Saloma, G. Bidan and E.M. Geniès, *Electrochim. Acta*, 34 (1989) 117.
- [9] D. Delabouglise and F. Garnier, *Synth. Met.*, 39 (1990) 117.
- [10] F. Cardielli, S. Lanzillo and O. Pieroni, *Macromolecules*, 7 (1974) 174.
- [11] J.F. Moore, C.B. Gorman and R.H. Grubbs, *J. Am. Chem. Soc.*, 113 (1991) 1704.
- [12] M. Yamaguchi, K. Omata and M. Hiram, *Chem. Lett.*, (1992) 2261.
- [13] T. Aoki, M. Kogai, K. Shinohara and E. Oikawa, *Chem. Lett.*, (1993) 2009.
- [14] E. Harlev and F. Wudl, in W.R. Salaneck, I. Lundström and B. Rånby (eds), *Conjugated Polymers and Related Materials. The Interconnection of Chemical and Electronic Structure*, Proc. Eighty-first Nobel Symp., Vol. 139, Oxford University Press, Oxford, 1993.

- [15] A. Delmotte, M.M. Bouman and E.W. Meijer, unpublished results.
- [16] A.F. Drake, P. Udvarhelyi, D.J. Ando, D. Bloor, J.S. Obhi and S. Mann, *Polymer*, 30 (1989) 1063.
- [17] R.L. Elsenbaumer, H. Eckhardt, Z. Iobal, J. Toth and R.H. Baughman, *Mol. Cryst. Liq. Cryst.*, 118 (1985) 111.
- [18] Y. Cao, A. Andreatta, A.J. Heeger and P. Smith, *Polymer*, 30 (1989) 2305.
- [19] Y. Cao, P. Smith and A.J. Heeger, *Synth. Met.*, 48 (1992) 91.
- [20] R. Sheldon, *Chem. Ind.*, (1990) 212.
- [21] P. Smith, personal communication.