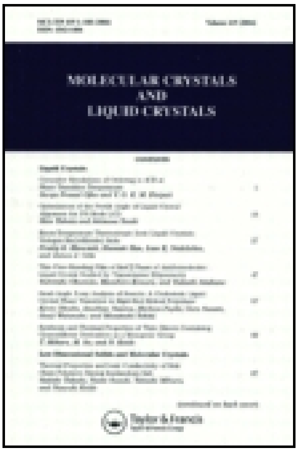
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 19 February 2013, At: 11:19
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Optimisation of the Electrosynthesis of Polythiophene and Polyselenophene Films

Claude Chorro [a] , Bertil Moukala [a] , Jean-Pierre Lere-porte [a] & Jean Petrissans [a]

[a] Laboratoire de Chimie Générale, Université de Montpellier, Place Eugène Bataillon, 34095, Montpellier, Cedex, 5, France

Version of record first published: 22 Sep 2006.

To cite this article: Claude Chorro , Bertil Moukala , Jean-Pierre Lere-porte & Jean Petrissans (1990): Optimisation of the Electrosynthesis of Polythiophene and Polyselenophene Films, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 199-205

To link to this article: http://dx.doi.org/10.1080/00268949008036043

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 199–205
Reprints available directly from the publisher
Photocopying permitted by license only
© 1990 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

OPTIMISATION OF THE ELECTROSYNTHESIS OF POLYTHIOPHENE AND POLYSELENOPHENE FILMS.

CLAUDE CHORRO, BERTIL MOUKALA, JEAN-PIERRE LERE-PORTE, JEAN PETRISSANS.
Laboratoire de Chimie Générale, Université de Montpellier,
Place Eugène Bataillon , 34095 Montpellier Cedex 5 , France.

Abstract Conditions were improved in the electrochemical preparation of polythiophene and polyselenophene films in order to increase the conductivity and stability of doped films and to improve the reproducibility of the synthesis. The effect of the following parameters were studied:nature and temperature of the solvent, ageing of the solution, nature of the doping anion, nature of the monomer, thickness of the film.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

INTRODUCTION

Conducting polymers have constitued a growing field of science and engineering for ten years since polyacetylene was discovered to be higly conducting upon doping with,for example,iodine and arsenic pentafluoride[1]. After this discovery a large set of conductive polymers has been synthesized by chemical or electrochemical methods : polyaromatics (polyparaphenylene, polyparaphenylene sulfide), polyheterocycles (polypyrrole, polythiophene, polyselenophene). Polyheterocycles such as polypyrrole, polythiophene and polyselenophene are interesting because they are easily synthesized as free standing films by electrooxydation of a monomer dissolved in an electrolytic solution. The resulting polymers are made to be highly conducting by in situ doping with anion species of the supporting electrolyte.

Industrial applications of such compounds require high conductivity, stability toward atmosphere and reproducibility of the synthesis. Optimisation of the conductivity of polythiophene (PT) and polymethylthiophene (PMeT) electrochemically generated has been intensively studied by several research groups[2-5] . In France , Garnier and Col[6-11] have improved the conductivity of PMeT by varying experimental conditions such as monomer concentration, thickness of the film and

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

electrolyte anion. To our knowledge, the problem related to the stability and reproducibility has received less attention. We present in this paper first results on the optimisation of the electrosynthesis of PT and polyselenophene (PSe) films in order to improve simultaneously the conductivity and the stability of the compounds and the reproducibility of these synthesis. We report results concerning the effect of the following parameters:

- nature and temperature of the solvent,
- nature of the doping anion,
- nature of the monomer,
- ageing of the solution;
- thickness of the film.

EXPERIMENTAL SECTION

The electrochemical synthesis was performed in an one-compartment cell using an EG&G potentiostat model 363 under computer control. The working and counter electrodes were platinum sheets (2x2.5 cm) placed at 1.8 cm and the anodic potential was measured versus an $Ag/AgNO_3$ (10^{-2}M) electrode. The platinum sheets were carefully polished with Al_2O_3 (Presi , 1 μm) after each synthesis. Oxygen was excluded from the electrochemical cell by a nitrogen flow. Electropolymerisation of the monomer dissolved in the electrolytic solution was performed at 1.3 V versus an $Ag/AgNO_3$ (10^{-2}M) electrode. The integrated charge (Q) passed during film growth was used to monitor the thickness of the deposited film. The following relation was used : e (μ•m) = 2.5xQ (Cb/cm^2). The DC conductivity of doped free standing films was measured using the conventional four probes methods: four copper wires were attached to the doped film using " electrodag". The film thicknesses were determined with a " Heilderham" thickness monitor.

RESULTS AND DISCUSSION

Nature of the solvent

We have oberved, in agreement with published data[4], that PT films prepared in acetonitrile adhere firmly to the electrode and detach only with great difficulty. The quality of the samples obtained in this solvent is not easily reproduced: the conductivity of the films prepared

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

under similar conditions can vary from 10^{-1} to 100 $\Omega^{-1}.cm^{-1}$. The films are , in addition, not homogeneous: the side in contact with the electrode is smooth and shiny and that which is in contact with the solution is rough and irregular. The study of the photoluminescence[12] confirms the pronounced lack of homogeneity of the two sides and lead us to conclude, in agreement with Garnier and Col[6] that the quality of the film degrades progressively during the period of growth.

The reproducibility of the synthesis is clearly improved when nitrobenzene is used as a solvent. The measured conductivities varied from 80 to 100 $\Omega^{-1}.cm^{-1}$. The films appear more homogeneous, the two sides are shiny. The study of the photoluminescence reveals[12], moreover, that the differentiation of the two faces is less pronounced that observed for films prepared in acetonitrile.

Temperature of the solvent

Tanaka[13] has reported that the temperature of the electrolytic solution has an effect on the conductivity of PT films. In accord with the results of these authors, we have found that a low temperature(5°C) improves the conductivity(Table I) and the mechanical properties of PT films.

TABLE I Conductivity of PT films prepared at 40, 20 and 5°C in nitrobenzene.

Temperature (°C)	Conductivity ($\Omega^{-1}.cm^{-1}$)
40	very weak
20	10-40
5	85-100

Infrared spectra of PT films prepared at 40, 20 and 5°C are very similar. We have not observed, as mentioned by Tanaka[13], absorptions which can be associated with cross-linking of polymer chains.

Ageing of the solution

Table II shows the conductivity of PT films prepared in potentiostatic conditions (1.3 V versus Ag/$AgNO_3$ (10^{-2}M) electrode) using the same electrolytic solution ($N(Bu)_4ClO_4$ in nitrobenzene at T=5°C), Before each synthesis the platinum sheets were carefully polished with Al_2O_3.

It can be noted that the conductivity values are nearly the same. As pointed by Delabouglise[14] the formation of oligomers should lead to a decrease of the conjugation length and conductivity.

TABLE II Conductivity of PT films as a function of the number of films synthesized from the same momomer solution.

Film number	Conductivity ($\Omega^{-1}.cm^{-1}$)
1	94
2	85
3	110
4	93
5	107

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

Nature of the doping anion

Marque and Col[9] have reported that the nature of the doping anion plays a determining role in the structure of the polymer during its synthesis The best electrochemical properties are obtained for PF_6^- and decrease in the order PF_6^- , ClO_4^- , BF_4^- and $CF_3SO_3^-$. According to these results, we have observed that the conductivity of ClO_4^- doped films is larger than BF_4^- doped films. However it seems quite difficult , at the present, to attribute exlusively this change to the doping anion, excluding any contribution of water which can be present in various amounts in electrolytes or solvents. Evolution of the conductivity of BF_4^- and ClO_4^- doped films exposed to air is shown in figure 1. In both cases, we note a decrease in the conductivity values versus time. The rate of this decrease is larger for films doped with BF_4^- anions. Contrary to the observations of Hotta[15] this evolution is found irreversible. We have not observed an increase in the conductivity when a film exposed to the atmosphere is left in dry air.

Nature of the monomer

PT films can be elaborated by electrochemical oxidation of a monomer such thiophene or 2,2'-bithiophene. For some authors[16-17] , the use of 2,2'-bithiophene improves the quality of PT. This result is contested by Roncali and Col[8].

We prepared under potentiostatic conditions self-supporting films

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

using nitrobenzene as a solvent, $N(Bu)_4ClO_4$ as an electrolyte and thiophene as a monomer. The conductivity of these films is close to 100 Ω^{-1}.cm^{-1} and their polymerisation length (Ndp), determined by infrared spectroscopy using the procedure described by Furakawa [18], has a value of 70 thiophene rings. In accord with the results published by Roncali[8] we have oberved during the electropolymerisation of 2,2'-bithiophene, the formation of a very thin film which is gradually covered by a granular deposit. The conductivity(σ) and the polymerisation length are low ($\sigma=10^{-2}$ Ω^{-1}.cm^{-1}), Ndp = 30). The polymerisation of selenophene a monomer whose conjugation seems higher than that of thiophene, leads to a self suporting film which has a short polymerisation length (10) and a very poor conductivity (10^{-3} Ω^{-1}. cm^{-1}).

The decreade in the polymerisation length leads to an increase of the interchain jump , factor which limits the conductivity. In conclusion thiophene is the best choice of monomer.

Thickness of the film

According to Yassar and Col.[11], the conductivity of PMeT films prepared in galvanostatic conditions is notably diminished when their thickness increases. Taking into account these results, we have synthesized PT films of different thicknesses (.5 to 3 μm) at a controlled intensity. The conductivity decreases with the thickness: σ = 20, 31 and 43 Ω^{-1}.cm^{-1} for e = 2 , 0.8 and .5 μ.m. In addition, we have studied the stability of these films when they are exposed to the atmosphere (figure 1). It clearly appears that the thinnest films lose their conductive properties the most rapidly.

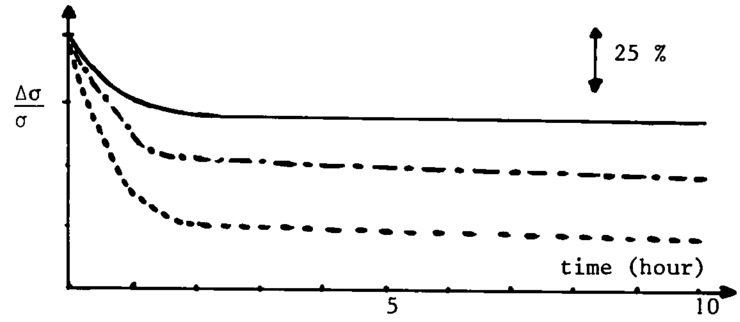


FIGURE 1 Conductivity change of PT films exposed to air. ••• : BF_4^- doped , l= 2 μm; — : ClO_4 doped, l= 2 μm; - • - : ClO_4 doped, l=.3μm.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013

We have not observed a significant variation in the conductivity of the films, whether thick or thin , when they are prepared in potentiostatic conditions. Our initial results reveal, in effect, that the conductivity of these films is practically constant (80 to 100 $\Omega^{-1}.cm^{-1}$) when their thicknesses increases from 2 to 4 µm. The conductivity is superior to that of films with the same thickness elaborated in galvanostatic conditions.

CONCLUSION

We conducted these various assays in order to improve the electrosynthesis of PT and PSe films. The results lead us to formulate the following conclusions:

- the choice of a solvent such as nitrobenzene improves the reproducibility of the synthesis and the homogeneity of the film. The conductivity is increased when the synthesis is carried out at a low temperature (5°C). Using ClO_4^- as dopant anion improves both conductivity and the stability of the films in the atmosphere. The ageing of the solution doesn't seem have an effect on the quality of the films. It therefore appears that the best environment for the preparation of these films is a solution of $N(Bu)_4ClO_4$ in nitrobenzene at 5°C,
- the increase in the conjugation of the monomer leads to a decrease in the polymerisation length and very low conductivity. Thus, the measured conductivities of polybithiophene and polyselenophene are inferior to those of polythiophene ,
- the conductivity of PT films formed galvanostatically, varies a a little with the thickness. The thin films are the best conductors but prove to be unstables in the atmosphere. On the other hand, the thickness of the films does not seem to affect their conductivity when they are prepared at a controlled potential. This method of electropolymerisation is, in our hands, the best choice.

REFERENCES

1. T.A Skotheim, Handbook of conducting polymers,(Marcell Dekker, New-York, 1986)
2. S. Tanaka, M. Sato and K. Kaeriyama, Makromol. Chem., 185, 1295(1984).
3. K. Kaneto, K. Yoshino and Y. Inushi, Jap. J. of Appl. Phys.,21(9), L567 (1982).
4. S. Hotta,T. Hosaka and W. Shinotsuma, Synth. Metals , 6 ,69 (1983).

5. R.J. Waltman, J. Bargon and A.F. Diaz, J. Phys. Chem., 87, 1459(1983).
6. G. Tourillon and F. Garnier, J.Phys. Chem., 87, 2289 (1983).
7. J. Roncali and F. Garnier, New J. Chem.,10(4-5), 237(1986).
8. J. Roncali, F. Garnier, H. Lemaire and R. Garreau, Synth. Met. ,15, 323 (1986).
9. P. Marque,J. Roncali and F. Garnier, J. Electroanal. Chem., 218,107 (1987)
10. J. Roncali, M. Lemaire, R. Garreau and F. Garnier, Synth. Met.,18 ,139 (1987).
11. A. Yassar, J. Roncali and F. Garnier, Macromolecules, 22, 804 (1989).
12. J.L Sauvajol, D. Chenouni, J.P Lère-Porte,Cl. Chorro, B. Moukala, and J. Petrissans, Synth. Met. (1990), on press.
13. K. Tanaka,, T. Schichiri and T. Yamabe, Synth. Met., 16, 207 (1986).
14. D. Delabouglise, R. Garreau, M. Lemaire, J. Roncali, New J. Chem., 12, 155(1988).
15. S. Hotta, " Syntheses and electronic properties of polythiophene and its derivatives ", P.H.D, Osaka (1988).
16. C. Chung, J.H Kaufman, A.J Heeger, F. Wuld, Phys. Rev. B,30, 702 (1984).
17. M.A. Druy, A. Seymour, Proceedings of the International Conference on the physics and chemistry of conducting polymers, J. de Physique, C3, 395 (1983).
18. Y. Furukawa, M. Akimoto, I. Harada, Synth. Met., 18, 189(1987).

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:19 19 February 2013