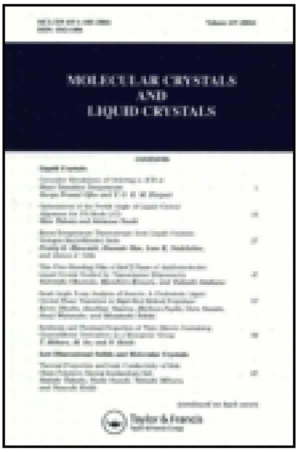

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Langmuir Blodgett Films with Thiophene Based Polymers

G. Bajo [a] , A. Bolognesi [a] , S. Destri [a] , Z. Geng [a] & M. Porzio [a]
[a] Istituto di Chimica delle Macromolecole, Via E. Bassini, 15 20133, Milano, Italy

To cite this article: G. Bajo , A. Bolognesi , S. Destri , Z. Geng & M. Porzio (1993): Langmuir Blodgett Films with Thiophene Based Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 91-96

To link to this article: http://dx.doi.org/10.1080/10587259308032181

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 91–96
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

LANGMUIR BLODGETT FILMS WITH THIOPHENE BASED POLYMERS

G. BAJO, A. BOLOGNESI* , S. DESTRI, Z. GENG, W. PORZIO
Istituto di Chimica delle Macromolecole, Via E. Bassini 15
20133 Milano - Italy

Abstract Poly(3-alkylthiophenes) have attracted great attention in the new generation of organic materials for electronics due to their processability. Particularly it is necessary for the preparation of high quality material suitable for electronic application to have well oriented polymers with a well defined molecular architecture. In this view we have synthesized different kind of polyalkylthiophene and we have tested the possibility to obtain improved materials by using the Langmuir Blodgett technique.

INTRODUCTION

Polyenic systems such as poly(3-alkylthiophenes) (PATs) are object of study for their interesting electrical and electronic properties [1] The easy processability of this kind of materials has opened new possibilities of applications in the electronic field where thin films with a well defined thickness and structure are required. The Langmuir Blodgett technique offers a valid tool for preparation of molecular architecture in a controlled way : by means of this technique monomolecular layers are subsequently deposited onto substrates of different nature making it possible the control of the structure of a material at the molecular level[2] The aim of this work is to present some data concerning the preparation of LB multilayers with polymers based on 3-alkylthiophene as repeating unit. Some chemical modification of poly(3-alkylthiophene) were necessary in order to have macromolecules preserving the polyenic backbone system but showing higher tendecy to form stable and transferable monolayers.

EXPERIMENTAL

Poly(3-decylethoxythiophene) 1 was synthesized according the same polymerization procedure described in literature [3] for preparation of PATs. Molecular weight of 1, obtained by GPC on a Waters 600 E instruments, was 8.000 (referred to standard polystyrene). LB multilayers were performed with a Lauda trough computer controlled. The subphase was twice distilled water further purified with a

Milli-Q system . Solution of 1 in chloroform were prepared and spread over the subphase. Clean microscope glass slides were rendered hydrophobic by immersion in a solution of dimethyl-dichlorosilane in chloroform (2% vol). UV-vis spectra were detected with a Cary 2400 Spectrometer. XRD spectra were recorded with a computer controlled Siemens D-500 diffractometer equipped for thin films investigation.

RESULTS AND DISCUSSION

It has been proved by some authors[4,5] that PATs alone are not able to give stable and transferable monolayers on the water surface. Only by mixing PATs with arachidic acid (AA) in a wide range of molar ratio stability is reached on water subphase containing $CdCl_2$. We were able [5] to prepare good quality multilayers with a molar ratio of 3/1 (AA/poly(3-decylthiophene)) which were investigated by UV-Vis spectroscopy and XRD techniques. The data so far obtained were consistent with the following model: each layer is formed by a mixture of AA and poly(3-decylthiophene) and the two components are completely segregated . Moreover it was shown [5] by means of UV-Vis spectroscopy that the polymer in the LB film has a more extended conformation with respect to the conformation the polymer has in cast film. The possibility of obtainig high quality LB multylayers was investigated also with poly(3-decylthiophene-2,5-diylvinylene) which was recently prepared in our group [6] . On our opinion the introduction of a double bond between the thiophene units give higher flexibility to the chain with respect to poly(3-decylthiophene) making the polymer more suitable for LB preparation.

But in this case also success was obtained only by mixing the polymer with AA. In addition an easy oxydation of the polymer was observed due to the high surface exposition to air, water and light [6] during deposition.

In the above mentioned cases only a partial goal was reached because even if the transfer of the monolayers from the water surface to the substrate is good (the transfer ratios are 1) and the polymers have a higher conjugation length in the LB multylayers, these materials cannot be proposed for any electrooptical application due to two reasons: - each multylayer is formed by a mixture of a polymer which is conducting (on doping) and an insulating compound (AA) resulting, from the electrical point of view, in a material with poor conduction quality; - within each layer the two compound are completely segregated and scattering phenomena are expected for example in transmission of light [7] . For these reasons we tried to further modify the polymer in order to have a polyenic system which alone can form LB film.

Preserving the polythiophene backbone was necessary in order to maintain the polyenic backbone (responsible for the electrical and electronic properties). So we thought to modify the side chain by introduction of an oxigen atom in order to improve the polarity of the polymer synthesizing 1. This chemical modification was proved to have a strong influence on the isotherm of the polymer on water surface which results different from those found for the two above mentioned polymers. As can be seen (Fig 1) a sudden increase of the surface pressure is observed for value of area per molecule around 22 A^2. The value of area per molecules extrapolated at 0 pressure is 19 A^2 which is near to the value found by Leclerc et al [8] for poly(3,4-dibutoxythiophene) (20 A^2). These data strongly suggest the idea of an horizontal disposition of the backbone of the macromolecules respect to the water surface the side chain being probably oriented in a way such as to allow polar interaction of the oxigen with the water surface. The shape of the isotherm does not significantly change with temperature ranging from 5°C to 20°C.

The stability of the monolayers on water surface was good in order to have deposition in the region between 15 and 17 mN/m. Deposition does not occur in a regular way. In fact in the first dipping no appreciable deposition was observed on the hydrophobic glass substrate, while in the subsequent upstroke deposition occurred on both side of the substrate. After this first cycle transfer from the water surface was succesfull only on the substrate face in front of the moving barrier and the kind of deposition was Z type (transfer only in the upstroke cycle).

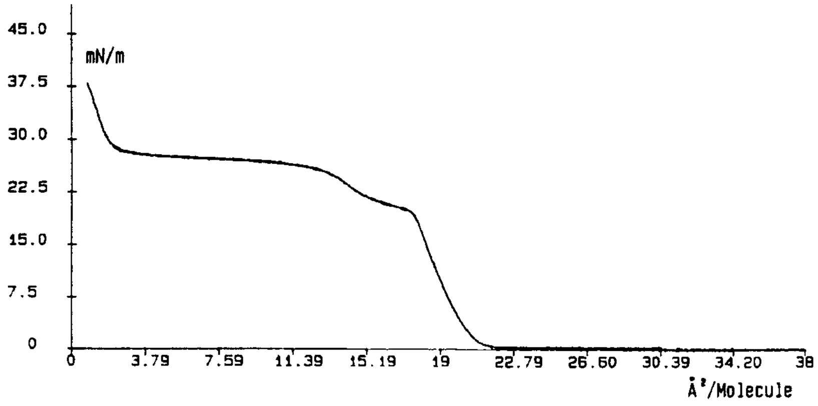

FIGURE 1 Isotherm of 1 at 15°C

Different substrate are under investigation in order to see the effect of polarity of the substrate with respect to the kind of deposition. Deposition up to 30-36 layers was possible with a transfer ratio near to 1 (considering deposition only on one side). After 36 layers the deposition ratio decreased indicating a progressive decreasing of the quality of the layers. In Fig. 2 the UV-Vis spectrum of 30 multylayers of 1 is reported together with its spectrum in solution and in form of film cast from solution.

As can be seen no appreciable difference can be observed between the maximum of the absorption of the spectrum of the multylayers and that of cast film indicating that in both the situation the polymeric chain have the same conjugation length. This is, as far as we know, the first example of LB multylayer formed by polyalkylthiophene alone in which the polymer exhibits the same situation found in film cast from solution.

XRD data were obtained by investigating only the face in front of the moving barrier of the trough. Surprisingly the only observed d is strictly dependent on the temperature of observation and the annealing time of the sample varying from 30 A to 45 A at 25°C and 15°C respectively. The explanation of this interesting phenomenum is strictly connected, on our opinion, with the behaviour of the polymer side chains which, upon heating or cooling, change their steric hindrance thus influencing the interlayer packing. The large FWHP observed indicates that the order perpendicularly to the substrate is not high, extendig over 3 layers on the average.

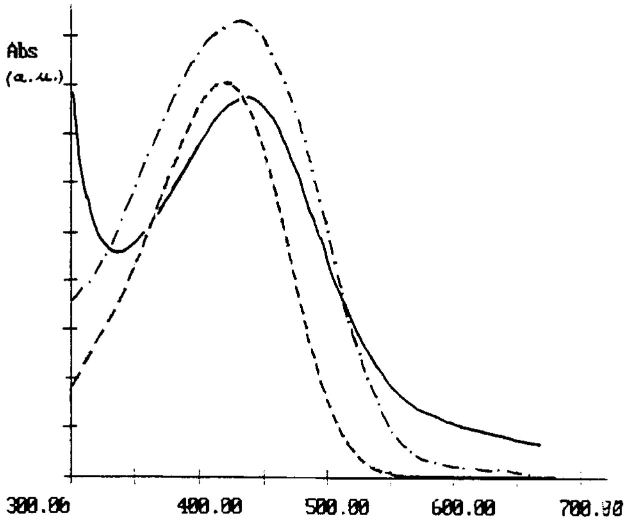

FIGURE 2 UV-Visible spectra of <u>1</u>: LB multylayers (full line), chloroform solution (dotted line), cast film (points and line)

Works are in progress in order to improve the quality of the films by changing the substrate and characterize the electrical properties of the obtained multylayers.

This work was partially supported by Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate of CNR, Rome, Italy

REFERENCES

1. For a comprehensive overview on poly(3-alkylthiophenes) see Synth. Met. 41-43 (1991
2. G. Roberts, in Langmuir Blodgett Films (Plenum Press 1990)
3. M. Kobayashy, J. Chen, T.C. Chung, F. Moares, A. J. Heeger, F. Wudl, Synth. Met. 9, 77(1984)
4. I. Watanabe, K. Hong, M.F. Rubner, Langmuir 6, 1164(1990)
5. G. Bajo, A. Bolognesi, M. Catellani, S. Destri in Materials for Photonic Devices, edited by A. D'Andrea et al. (World Scientific 1991), p. 270
   W. Porzio, A. Bolognesi, S. Destri, M. Catellani, G. Bajo. Synth. Metals, 41, 537, (1991).
6. R. Galarini, A. Musco, R. Pontellini, A. Bolognesi, S. Destri, M. Catellani, M. Mascherpa, Z. Geng, J. Chem. Commun. 369 (1991)
7. E.Castellucci private communication.
8. C. Callender, C.A. Carere, G. Daoust, M. Leclerc, Thin Solid Films 204, 451(1991)