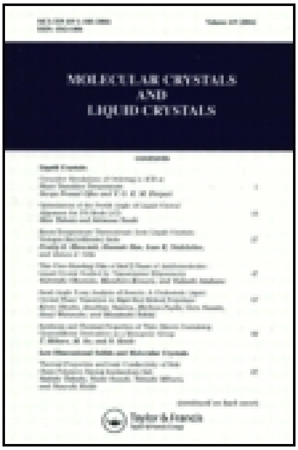

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On Structure and Properties of Polypyrrole Alkyl-Sulf(on)Ates

Wolfgang Wernet [a], Michael Monkenbusch [a] & Gerhard Wegner [a]

[a] Institut für Makroraolekulare Chemie, Hermann-Staudinger-Haus, Universität Freiburg, D-7800, Freiburg, Germany

To cite this article: Wolfgang Wernet, Michael Monkenbusch & Gerhard Wegner (1985): On Structure and Properties of Polypyrrole Alkyl-Sulf(on)Ates, Molecular Crystals and Liquid Crystals, 118:1, 193-197

To link to this article: http://dx.doi.org/10.1080/00268948508076210

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 193-197
0026-8941/85/1184-0193/$10.00/0

Printed in the United States of America

ON STRUCTURE AND PROPERTIES OF POLYPYRROLE ALKYL-SULF(ON)ATES

WOLFGANG WERNET, MICHAEL MONKENBUSCH, GERHARD WEGNER
Institut für Makromolekulare Chemie, Hermann-Staudinger-Haus, Universität Freiburg,
D-7800 Freiburg, Germany

Abstract Tenside anion "doped", highly conducting polypyrroles (PPY) have been grown electrochemically from aqueous electrolytes. The influence of the electrolysis parameters on the conductivity have been investigated. The X-ray diffraction patterns allow to derive a structural model.

INTRODUCTION

The use of (sodium) alkyltensides as "dopands" allow to grow high quality conducting PPY films from non toxic aqueous electrolytes. The electrical and the mechanical properties of these films are comparable to those grown under conventional conditions.[1,2]

SYNTHESIS

The electrolyte consisted of triple destilled deoxygenated water with 2 vol.% pyrrole 0.1 mol/l of one of the recrystallized tensides shown in table 1 and a sodium phosphate buffer to control the pH-value.
Oxidized PPY films were prepared by drawing an anodic current at constant current density through a disk shaped Pt-electrode. Stoichiometries from elemental analysis and room temperature conductivities are shown in table 1.
The room temperature conductivity[3] of the resulting films is rather sensitiv on different electrolysis parameters. The most drastic influence is effected by the pH-value of the electrolyte. The pH-value was adjusted using a phosphate buffer in a total concentration of 0.3 mol/l. Fig. 1 shows the variation of the conductivity, σ (300K), of PPY-SDS films, due to variation of pH. As can be seen there is a plateau of optimal pH-value in the range from $2<pH<5.5$.

TABLE I

tenside	$\sigma_{RT,max}$/S/cm	d(n)/nm	stoichio-metry(a)	anion weight fraction(%)
$H(CH_2)_{12}$-OSO_3^-	80	3.54	3..4:1	51.5
$H(CH_2)_{16}$-OSO_3^-	5	-	3.8:1	56.5
$H(CH_2)_4$-SO_3^-	5-10	1.94	3.5:1	37.5
$H(CH_2)_6$-SO_3^-	70	2.34	3.5:1	42.1
$H(CH_2)_8$-SO_3^-	160	2.69	3:1	49.7
$H(CH_2)_{10}$-SO_3^-	50	3.22	3:1	53.1
$H(CH_2)_{16}$-SO_3^-	-	4.14	3.9:1	54.6
SO_3^--(CH_2)-SO_3^-	25	1.96	8:1	36.5
$H(CH_2)_8OPO_3H^-$	12	2.46	4:1	43.1
$H(CH_2)_{10}$-OPO_3H^-	20	3.07	4:1	47.2

(a) Per unit there is up to one oxygen and up to two hyrogen in excess in the samples.

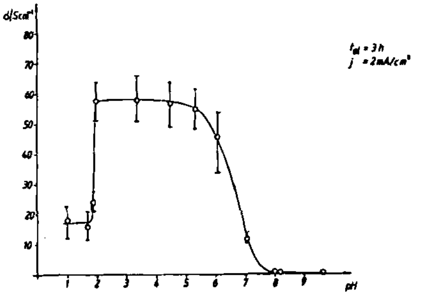

FIGURE I

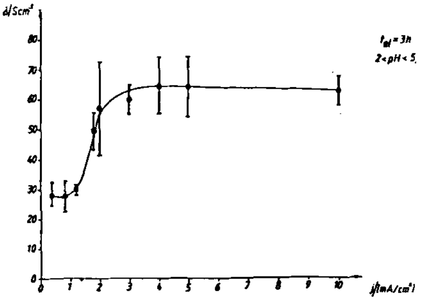

FIGURE 2

In more acid solutions protonation of pyrrole and subsequent oligomerization leads to products with saturated rings[4]. We believe that the copolymerization of these oligomers with pyrrole yields less conducting films.

Whereas in more basic environment the deterioation of σ may be a result of the reduced overvoltage for oxygen formation. Fig. 1 explains the large scatter of σ-values of films grown from electrolytes with a starting pH around 7.

Fig. 2 illustrates the influence of the electrolysis current density, j, on σ, it increases by more than a factor of 2 if the current density is raised from values below 1 mA/cm^2 to values above 2 mA/cm^2. The saturation effect which starts above 2 mA/cm^2 is probably due to self limitation of the effective current density by the onset of dentritic growth on the top of the film, thus increasing the surface. The yield of polymer is completely independent of j in the range up to 10 mA/cm^2.

Fig 3 shows the dependence of σ (300K) on the electrolysis temperature. At low temperatures the decreasing solubility of the tenside deterioates the result.

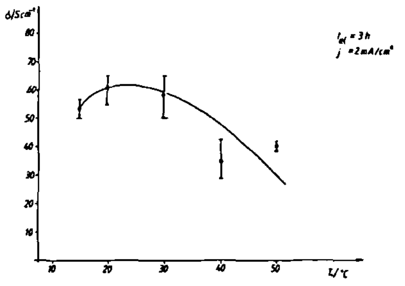

FIGURE 3

At high temperatures the increase of side reactions may probably causes the conductivity drop.

ELECTRICAL AND ELECTROCHEMICAL PROPERTIES

Fig. 4 (positiv potential) shows a cyclic voltammogramm of the beginning of the synthesis. The anodic current corresponds to polymer formation. The absence of a reduction peak even at high scan rates indicates the quick irreversible formation of the polymer. The left side of Fig. 4 shows electrochemical cycles on the oxidized PPY film (tenside = oktanesulfonate) immersed in an aqueous solution containing only the tenside as supporting electrolyte. Starting from the oxidized PPY one observes the reduction peak at -0.75V. The back sweep to the oxidized state reveals only a very broad bump. The charge flown during reduction is about 8.4% of the charge used to synthesize the film. 57 % of the reduction charge is retransfered during subsequent oxidation. Further cycles are indicated by their cycle numbers (2,119,120). Cycle 120 was taken 24 h after cycle 119. Obviously the redox behavior is changed by cycling in a manner that partly relaxes after a rest period of several hours.

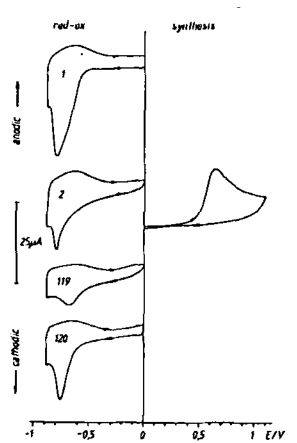

FIGURE 4

The temperature dependence of σ is similar to that of other conducting polymers and can be described by the Mott^5 model of variable range hopping, the slope of ln σ vs. $T^{-1/4}$ depends-like σ (300K)- on the preparation conditions. Samples with a ratio σ (300K)/σ(10K) as low as 1.4 could be achieved.^{6}

STRUCTURE

In contrast to X-ray diffraction for oxidized PPY complexed with small anions like BF_4^- the diffraction patterns of tenside containing PPY show a new intense small angle peak at $2\vartheta = 2^\circ$ to 5° ($\lambda = 1.542$, $Cu_K\alpha$) depending on the tenside anions. This is illustrated in Fig. 5 by the patterns from PPY-14-sulfonate (A) and from PPY-8-sulfonate (B). The long spacings (d-values) of these peaks have been determined by a fitting procedure taking into account the large disorder in our samples.[6] The ideal Bragg positions do not correspond exactly to the peak maxima. They are located at slightly lower scattering angles as shown by the black bars in Fig. 5. The spacings, d, are linearly correlated to the lenght of the alkyl chains, n, by

$$d(n) = (0.19\ n + 1.2)\ /\mathrm{nm} \qquad (1)$$

The spacing obtained for α,ω-decane-di-sulfonate ($SO_3^- -(CH_2)_{10}-SO_3^-$) is only 63 % of that calculated from formula 1. These observations indicate that

(i) tenside mono anions are incorporated in the polymer in double layered arrangements, because otherwise the slope of d(n) vs. n should be lower than $0.125/CH_2$-unit;

(ii) the residual distance for the ionic group and the PPY-chains is 1.2 nm;

(iii) difunctional tensides are incorporated in form of single layer structure elements.

These conclusions led us to the structure model depicted in Fig. 5. The short lines represent pyrrole chains which are seen along the chain axis. There is large disorder which is e. g. indicated by the fact that there are no higher orders of the small angle peak and by its shape. The order as idealized in Fig. 5 ranges only about 3 "lattice planes" in each direction .

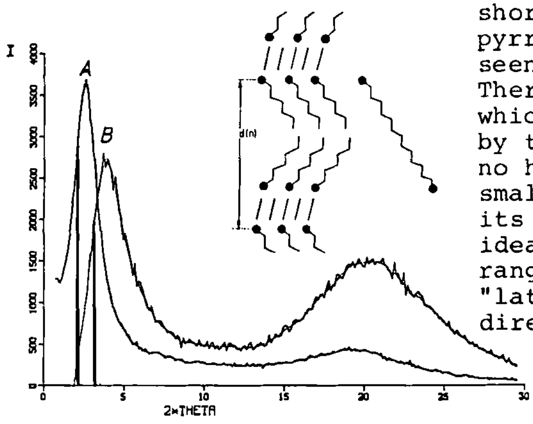

FIGURE 5

REFERENCES

1. A. F. Diaz, K. K. Kanazawa, J. Chem. Comm. 635(1979).
2. K. Kanazawa, A. F. Diaz, A. J. Logan, M. Krounbi, J. Bargon, J. of Molecular Crystals and Liquid Crystals, 83, 265 (1982).
3. L. J. van der Pauw, Philips Res. Rep., 13 (1) (1958).
4. H. A. Potts, G. F. Smith, J. Chem. Soc. 4018 (1957).
5. N. F. Mott, Philos. Mag., 19, 835 (1969).
6. W. Wernet, M. Monkenbusch, G. Wegner, Makromol. Chem. Rapid Commun., 5, 157 (1984).

ACKNOWLEDGEMENT

This work has been supported by the BMFT and the Quandt-Stiftung. The elemental analysis were performed at the BASF-AG Ludwigshafen.