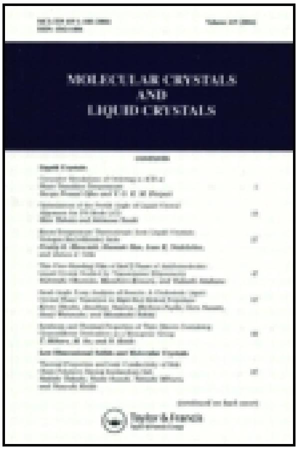

Molecular Crystals and Liquid Crystals

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

Electrochromic Effects of Conducting Polymers in Water and Acetonitrile

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To cite this article: Robert Bjorklund, Shalini Andersson, Stig Allenmark & Ingemar Lundstrωm (1985): Electrochromic Effects of Conducting Polymers in Water and Acetonitrile, Molecular Crystals and Liquid Crystals, 121:1-4, 263-270

To link to this article: http://dx.doi.org/10.1080/00268948508074873

Mol. Cryst. Liq. Cryst. 1985, Vol. 121, pp. 263-270
0026-8941/85/1214-0263/$15.00/0

Printed in the United States of America

ELECTROCHROMIC EFFECTS OF CONDUCTING POLYMERS IN WATER AND ACETONITRILE

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Abstract Polymer films of several N-substituted pyrroles were deposited on Au electrodes by electrochemical oxidation of the corresponding monomers in CH_3CN electrolyte. Cyclic voltammetry and light reflection measurements were performed in both CH_3CN and H_2O electrolytes after preparation. The results indicated that while all films were electrochemically and electrochromically active in CH_3CN, a variety of behavior was observed in H_2O. Poly-N-methylpyrrole films exhibited large optical changes in H_2O, whereas N-benzyl and N-tolyl derivatives were less active, and N-phenyl and N-bensoyl films were inactive.

INTRODUCTION

Polymer films produced by electrochemical oxidation of heterocycles are receiving increasing attention as electrode materials since the pioneering work at IBM with polypyrrole.[1-3] Several additional electroactive polymers have since been reported, including polymers of aniline[4], vinylcarbazole[5], azulene[6], and thiophene.[7-9] All such films have the property of being conductive and dark colored when oxidized, but become less conductive and lighter colored when neutralized.

With respect to electrochromism, it has been reported that derivatives of the parent monomers exhibit more favorable properties for practical applications. For example, films made from N-methylpyrrole[3,10] and 3-methylthiophene[9] have been found to be stable electrochromic films. We have therefore undertaken a study of films made from several N-substituted pyrroles. We have recently observed that poly-N-methylpyrrole films behave differently in CH_3CN and H_2O electrolytes.[10] The purpose behind the current study was thus to investigate several N substituted aryl derivatives in the two solvents to determine how electrochemical and optical properties are dependent on solvent. It is of particular interest how H_2O interacts with the films, since the starting monomers are all insoluble in H_2O.

EXPERIMENTAL

Pyrrole and N-methylpyrrole were purchased from Alfa Products. Both were distilled under vacuum and stored at -20°C prior to use. Other pyrrole derivatives were synthesized as described in the literature[11] and their structure and purity were confirmed by NMR. CH_3CN and Tetraethylammonium tetrafluoborate (Et_4NBF_4) were purchased from Alfa and Fluka.

Electrodes were prepared by vacuum depositing 50 Å Cr and 2500 Å Au onto microscope slides. The working area was a 0.5 cm^2 rectangle. Polymers were grown on the electrodes by oxidation in CH_3CN which was 0.1 M in Et_4NBF_4 and 0.05 M in monomer. Films of pyrrole, N-methylpyrrole, N-benzylpyrrole, and N-tolyl pyrrole were produced galvanostatically at a current density of 1 mA/cm^2 for 30-50 seconds. N-phenylpyrrole and N-bensoylpyrrole were polymerized at 1.8 and 1.4 V, respectively, versus a saturated calomel electrode (SCE). All films were grown to about 1000 Å thickness.

Films were rinsed in CH_3CN and dried in air after preparation. Simultaneous electrochemical and light reflection measurements were done in a 2 x 3 x 4 cm cuvette filled with 10 ml electrolyte (0.1 M Et_4NBF_4 in CH_3CN or H_2O). A Pt wire counter electrode and salt bridge were positioned 1 cm behind the working electrode. Potentials applied to the working electrode were controlled by a EG&G PARC Model 173 Potentionstat/Galvanostat. The potential sweep was controlled by a PARC 175 universal programmer. Reflection was studied by focusing a beam from an incandescent lamp on the 0.5 cm^2 polymer film. The reflected light was measured at about 70° with a photodiode.

Preparation and characterization of films were done with exposure to air except in the case of polypyrrole where N_2 was bubbled in the solutions. All voltages reported are versus SCE.

TABLE I Oxidation potentials and relative electrochromism of poly-N-substituted pyrrole films.

Substituent	Oxid. Pot. Volts [a]		Electrochrom. [b]	
	CH_3CN	H_2O	CH_3CN	H_2O
-H	-.15	-.15	.50	.25
$-CH_3$	+.52	+.38	.75	.75
$-C_6H_5$	+.75	--	.25	--
$-CH_2-C_6H_5$	+.70	--	.75	.25
$-CH_2-C_6H_4-CH_3$	+.60	+.60	.75	.25
$-CO-C_6H_5$	+.60	--	.25	--

a) film oxidation peak observed for a voltage sweep rate of 50 mV/sec.

b) scale 0 to 1, 1 corresponds to transition from fully transparent (neutral) to completely dark (oxidized).

RESULTS

In Table I we list the oxidation potentials of the polymer films in CH_3CN and H_2O electrolytes and the approximate maximum white light reflectance change observed when the voltage was swept in the two solvents. The reflectance change was the difference in reflectance on a scale where reflectance from a bare Au electrode was equal to 1 and reflectance when the light beam was blocked was 0 (illustrated in Fig. 1).

The first three polymers in the table, pyrrole, N-methylpyrrole, and N-phenylpyrrole, have been studied in CH_3CN by

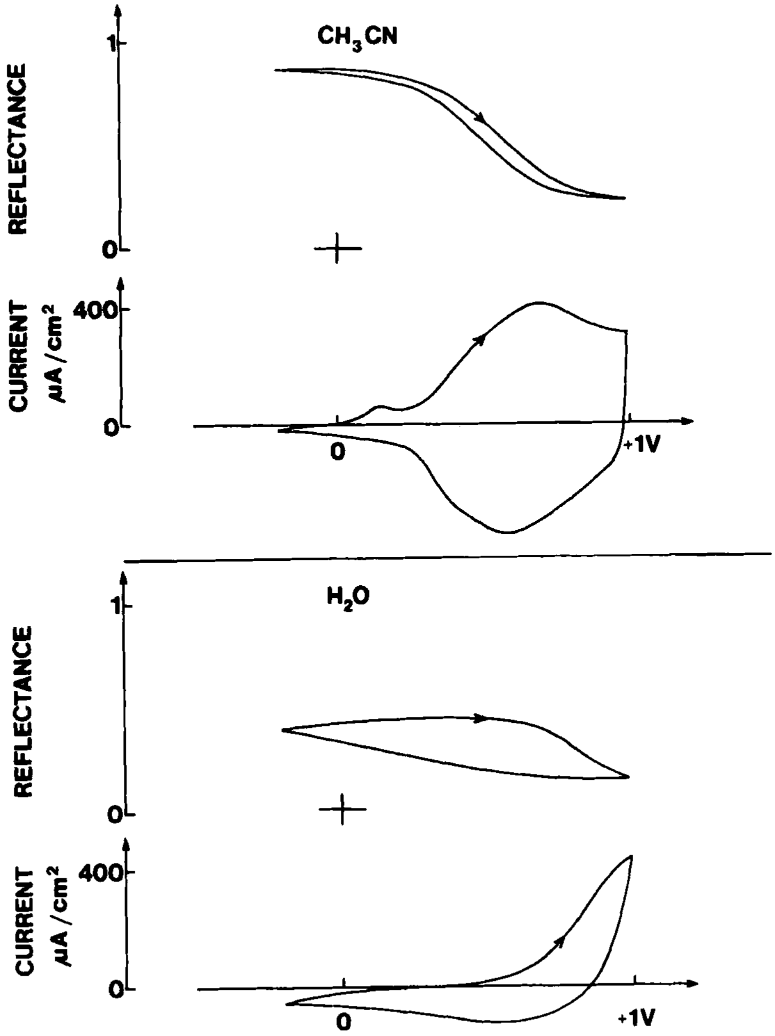

FIGURE 1 I-V and reflectance curves for N-benzylpyrrole films cycled in 0.1 M Et_4NBF_4 in CH_3CN and H_2O. Scale for reflectance curves was based on a value of 1 for reflectance from a bare gold electrode and 0 when light beam was blocked. Voltage sweep was 50 mV/sec.

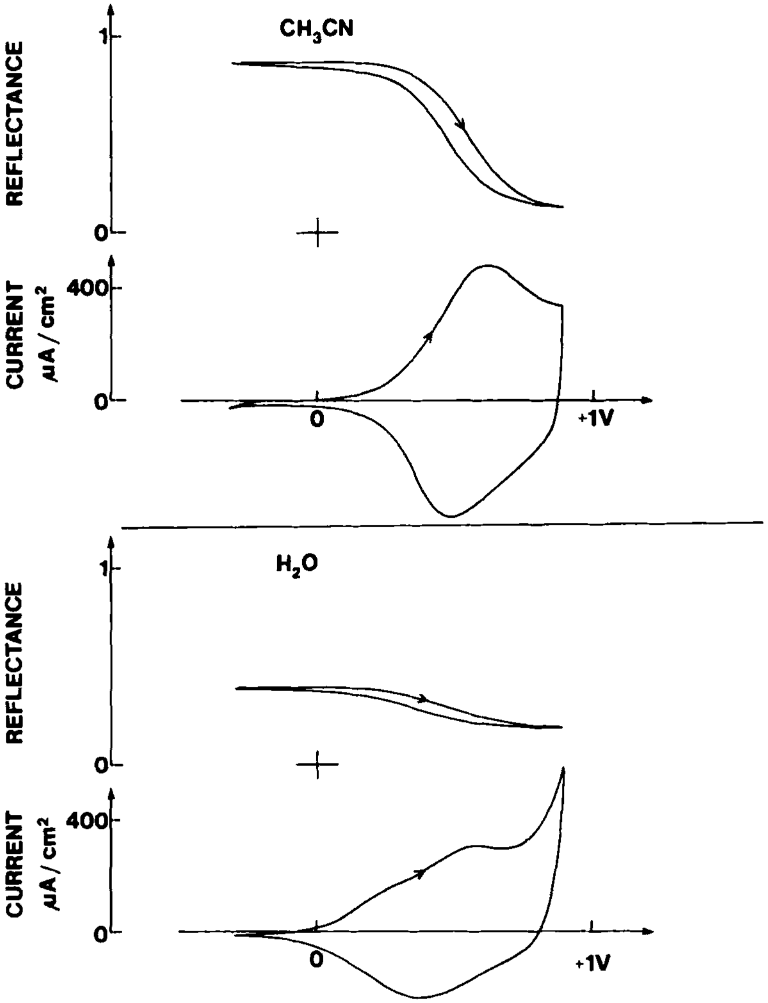

FIGURE 2 I-V and reflectance curves for N-tolylpyrrole films cycled in 0.1 M Et_4NBF_4 in CH_3CN and H_2O. Scale for reflectance curves was based on a value of 1 for reflectance from a bare gold electrode and 0 when light beam was blocked. Voltage sweep was 50 mV/sec.

IBM[1-3], and our oxidation potentials were in agreement with their previously reported values. Both pyrrole and N-methylpyrrole films could also be cycled in H_2O, but N-phenylpyrrole films showed no evidence for being electrochemically or optically active in H_2O. Largest reflectance change in both solvents was observed for N-methylpyrrole films.[10]

The last three films in the table have not been investigated previously. The first, N-benzylpyrrole, exhibited normal behavior in CH_3CN except for an additional small oxidation peak at +.15V(Fig. 1). However, in H_2O its I-V curve did not give evidence for oxidation-reduction, but some optical change was observed (Fig. 1). Considerably more hysteresis was observed for the reflectance curve in H_2O than in CH_3CN.

N-tolylpyrrole films were found to exhibit normal oxidation-reduction behavior in both solvents (Fig. 2). Reflectance change was greater in CH_3CN, but reflectance curves in both solvents had a similar hysteresis.

The final polymer listed in the table, N-bensoylpyrrole exhibited oxidation-reduction and electrochromism only in CH_3CN.

DISCUSSION

An earlier study by IBM of polymers prepared from N-alkyl substituted pyrroles has shown that certain properties, such as film oxidation potential in CH_3CN, varied systematically with substituent chain length.[12] Our own work with aryl substituted pyrroles did not find such trends in either CH_3CN or H_2O, but the results are useful with regard to understanding how the polymer film/electrolyte interface influences such properties as oxidation-reduction and electrochromism.

A model has emerged from numerous electrochemical studies on films immersed in CH_3CN which pictures a reversible flow of electrolyte anion species (such as BF_4^-) in and out of the polymer as the potential on the electrode is swept.[1-3] The anion species are not necessarily the ones added as electrolyte (e.g., BF_4^-) but can be some oxygen derived anion.[13,14] There has been evidence presented that cationic species are also included in the ion flow which accompanies oxidation-reduction.[3,10,15] Thus ion mobility and film solvation by the electrolyte are important factors in determining film properties.

With these factors in mind it can be concluded that N-methylpyrrole films are rather unique in terms of their behavior in both CH_3CN and H_2O electrolytes. As shown in Table I it is only N-methylpyrrole films which exhibited large optical changes in both solvents. We have discussed this phenomenon elsewhere,[10] and for this communication we will use poly-N-methylpyrrole's behavior as a standard to compare with the other polymers' characteristics.

Films of pyrrole exhibited electrochemical activity in both solvents, but relatively lower optical change in H_2O. It was also observed that the hysteresis of the reflectance curve in H_2O consisted of two parts, a narrow part when the film was oxidized and a thicker part when neutralized. We have previously shown that the hysteresis in such curves is dependent on ion flow in and out of films[10], it is not so surprising that the insulating (neutral) pyrrole film exhibited a larger hysteresis than the conducting (oxidized) film.[16] However, the fact that such behavior was not observed for polypyrrole in CH_3CN nor poly-N-methylpyrrole in both solvents is further evidence that the ion flow necessary for reversible oxidation-reduction occurs quite differently in H_2O and CH_3CN for some films.

Three of the aryl substituted polymers were not electrochemically active in H_2O (Table I). I-V curves were all similar to that shown for poly-N-benzylpyrrole in Fig. 1. The curve in H_2O was similar to what was observed for a bare Au electrode used as working electrode. This result can be taken as evidence that the polymers were porous to H_2O so that electrolyte could reach the metallic electrode, but that polymer solvation was not sufficient to allow oxidation-reduction. For poly-N-benzylpyrrole the situation was more complex since an optical change was observed in H_2O (Fig. 1). The large hysteresis in the curve indicates that ion flow was hindered compared to solvation in CH_3CN, but was at least sufficient to result in reversible electrochromism.

We conclude from our study that it is possible to obtain a variety of electrochemical and electrochromic properties of polymer films made from different N-substituted pyrroles depending on whether aqueous or organic based electrolytes are used as solvent.

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