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Optical properties of electrically conducting films formed by anodic oxidation of 1,2-di(2-thienyl)ethylene*

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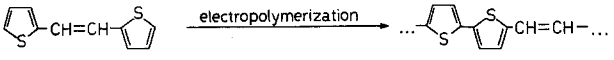
Poly(2,2′-bithienyl-5,5′-diylvinylene) (PBTV) films formed by anodic oxidation of 2×10^{-3} M solutions of trans-1,2-di(2-thienyl)-ethylene (trans-DTE) in acetonitrile were studied by voltammetry and ellipsometry. For the doped and undoped films, refraction indices and absorption coefficients in the wavelength range of 400–800 nm were determined as functions of thickness. Differences in the structure were found depending on the height of the oxidation potential. A decrease in thickness by doping was observed and is discussed in terms of a possible cis-trans isomerization. The optical spectrum of the undoped polymer showed a high degree of π-electron delocalization (high "degree of conjugation").

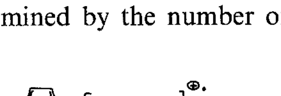
1. Introduction

In two previous papers [1, 2] the optical properties of electrically conducting films of poly(2,5-thiophenediyl) (PT) formed by anodic oxidation of thiophene in acetonitrile on platinum were investigated by ellipsometry. In the present paper optical properties of films of conducting polymers of poly(2,2′-bithienyl-5,5′-diylvinylene) (PBTV) formed by anodic oxidation of trans-1,2-di(2-thienyl)ethylene (trans-DTE) are described. There are remarkable differences in the properties of the two films. The process is schematically described by



DTE PBTV

with the polymer formed in its oxidized form. The charge is determined by the number of units of the type:



2. Experimental details

The experimental set-up for the investigation was the same as described in the previous papers [1, 2]. In some of the experiments, tetrabutylammonium perchlorate, instead of tetraethylammonium perchlorate, was used as electrolyte without any remarkable differences.

Trans-DTE was synthesized following a procedure described previously [3]. It was used, after careful purification by chromatography, in 2×10^{-3} M concentration.

3. Results

3.1. *Film Formation at 980 mV*

The film was grown by applying a cyclic potential-time program as described in Fig. 1. Starting at a potential of −100 mV against Ag/AgCl, the potential was linearly scanned up to +915 mV with a sweep rate of $30\,\mathrm{mV\,s^{-1}}$ and held at this potential for 5 s. At this potential an existing film was oxidized but no new film was grown. Then the potential sweep was continued up to +980 mV where it was held for 12 s. A new layer of film was grown at this potential increasing the overall thickness of the film. A cathodic sweep brought the potential back to −100 mV. In the cathodic scan from +980 mV to −100 mV the film was reduced. The current during this scan is plotted in Fig. 2a for different cycles. The reduction of the freshly grown film was followed by periodic oxidation/reduction without film growth leaving out the potential slope from 915 to 980 mV to carry out measurements at a different wavelength (Fig. 1c–d, 2b). The time, Δ*t*, necessary to change the wavelength was approximately 120 s. Simultaneously, the ellipsometric parameters were registered. This was repeated for wavelengths 800, 700, 600, 550, 500, 450 and 400 nm. Then,

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[*] This paper is dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

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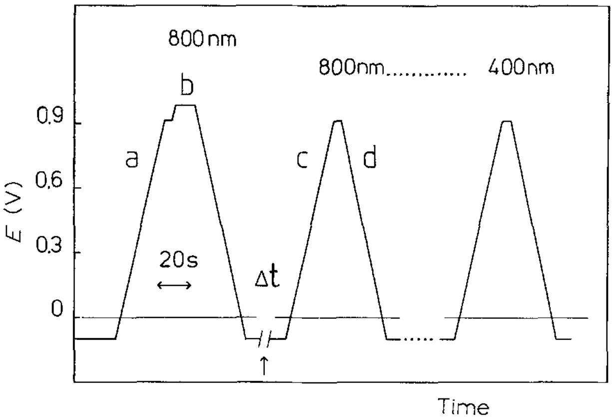


Fig. 1. Potential-time program for periodic anodic oxidation (a), film growth (b), and repeated oxidation/reduction without film growth (c, d). The potential-time diagram shown in the figure is referred to as one cycle in the text. Δ*t*, time to change wavelength (~2 min).

further film growth was initiated, repeating the initial potential variation (Fig. 1a–b, 2a) to increase the thickness of the film. The entire potential program of Fig. 1 is termed one cycle. The number in the figures and in the text refer to these cycles.

The ellipsometer values Δ and Ψ are plotted in Figs 3, 4 and 5 for various wavelengths. In Fig. 3b, in addition to the change of Δ and Ψ between −100 mV and +915 mV, the variation of the ellipsometric data during the growth of the film (Fig. 1, part a, b) is shown. In this case, after each cycle, the values Δ and Ψ differ by the change in film thickness while almost reversible behaviour is found for oxidation/reduction without film growth. The values of Δ and Ψ corresponding to the beginning of the potential scan and to the reverse of the scan direction belong to the reduced and to the oxidized form of the film, respectively.

Using the same procedure as described in the previous paper [1], the optical constants were calculated. For each wavelength, the experimental values of Δ and Ψ corresponding to different film thicknesses were fitted by a single pair of optical indices, *n* and *k*. A further criterion for the fitting procedure was that Δ and Ψ, measured at different wavelengths, had to be fitted by one thickness value. This procedure assumes that *n* and *k* do not depend on the thickness (isotropic and homogeneous film). The formal error of such a procedure is given by the step height of the fitting procedure, for instance $\Delta n = 0.01$, $\Delta k = 0.001$, $\Delta d = d/100$. The results (refraction index, *n*, and absorption coefficient, *k*) are shown in Fig. 6 for the oxidized form and in Fig. 7 for the reduced form of the film. While the oxidized form of the film does not show pronounced absorption, the appearance of the absorption maximum for the reduced form at 550 nm is characteristic. The ellipsometric thickness of the film versus the charge is shown in Fig. 8. The thickness calculated for the oxidized film is smaller than that for the reduced one. The charge in Fig. 8 was taken from the integration of the current in the cathodic scan (compare Fig. 2a). The average charge/thickness ratio for the oxidized and the reduced film is 19.7 μC nm^{-1}. The charge as a function of the number of cycles is shown in Fig. 9. While the charge needed for the growth of the film is almost constant (2.1 mC cm^{-2}) – except for the first scan – the charge for the reduction and oxidation of the film increases approximately linearly with the film thickness. The charge of the cathodic scan is smaller (15%) compared with the charge of the anodic scan, 15% of the current being lost during film oxidation.

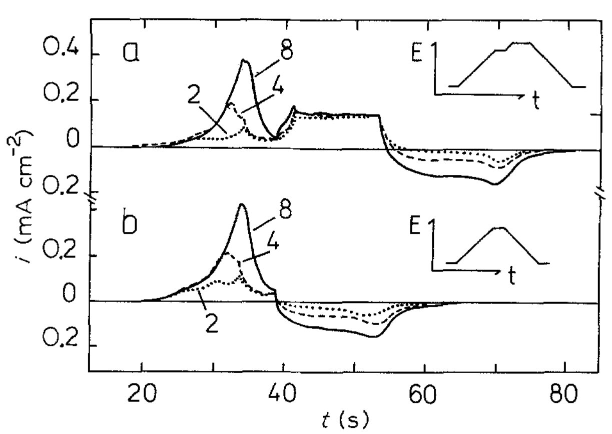


Fig. 2. Corresponding current-time plots for the oxidation/reduction cycles including film growth (a) and for oxidation/reduction without film growth (b) on platinum. The numbers refer to the successive cycles. 2×10^{-3} M DTE, 0.1 M (But)$_4$NBF$_4$, acetonitrile.

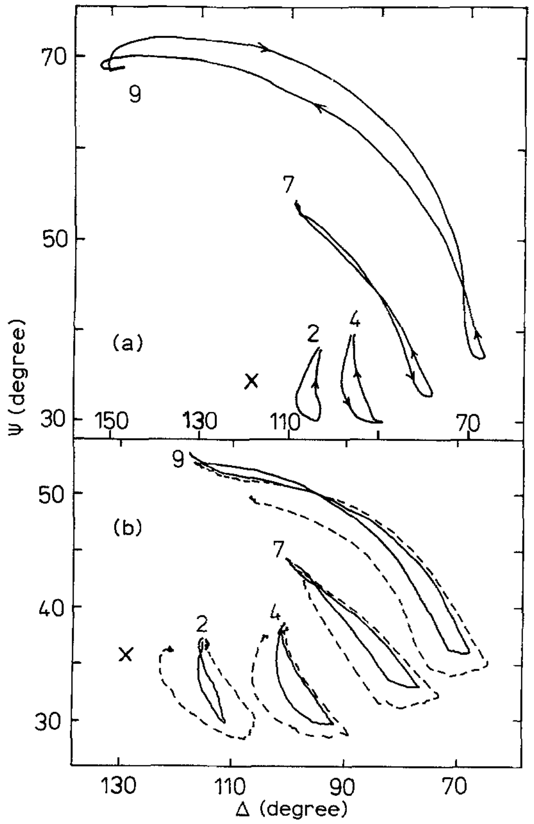


Fig. 3. Δ/Ψ plot for a potential scan from −100 mV to +95 mV and back to −100 mV for wavelengths 700 nm (a) and 800 nm (b). In (b), in addition to the reversible cycle for oxidation and reduction, a cycle including growths of the film (Fig. 2a) is shown (dashed line). The Δ/Ψ of the bare Pt electrode is given by (×).

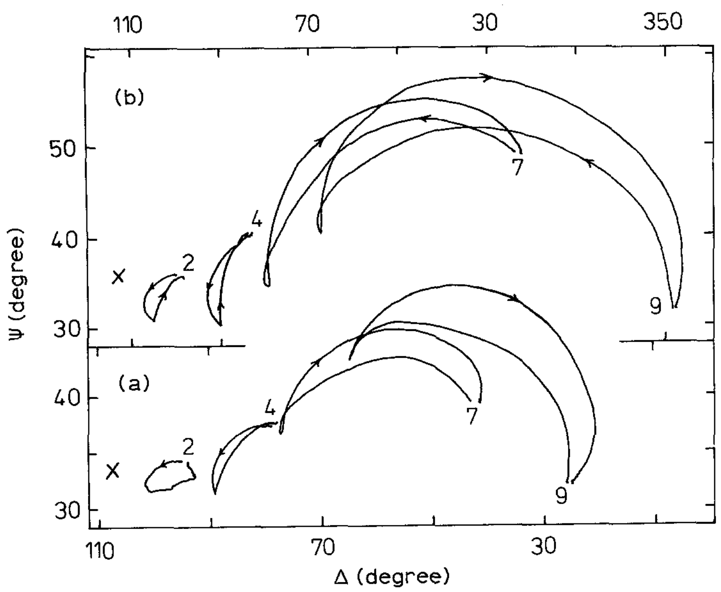


Fig. 4. Δ/Ψ plot for wavelengths 550 nm (a) and 600 nm (b).

3.2. *Film formation at 922 mV*

The cycles described in Fig. 2b were carried out with a decreased anodic oxidation potential of 922 V. The film formation is proved by ellipsometric measurements but the rate of film formation (current) was considerably smaller than at 980 mV (Fig. 2a). Δ and Ψ plots for three wavelengths are shown in Fig. 10. The evidence for film growth during each cycle is the hysteresis observed in the Δ/Ψ plots: at the end of each cycle there is a small deviation of the Δ/Ψ parameters from the values observed at the beginning of the cycle. It should also be mentioned that the Δ/Ψ variation in the reduction and oxidation scan is different when compared with the former experiment. The difference of a potential for film growth (980 and 922 mV) and a potential just below film growths (915 mV) can be described by the concept of overpotential. Of course the determination of a potential just below film growth is somewhat dependent on the experimental time scale which was of the order of 10^2 s. The potential has no real equilibrium value. The two cases can be distinguished as film formation at high (65 mV) and low (7 mV) overpotential.

Following the procedure described previously, refraction index, *n*, absorption coefficient, *k*, and thickness, *d*, of the film in the reduced and in the oxidized state were calculated. It is possible to use

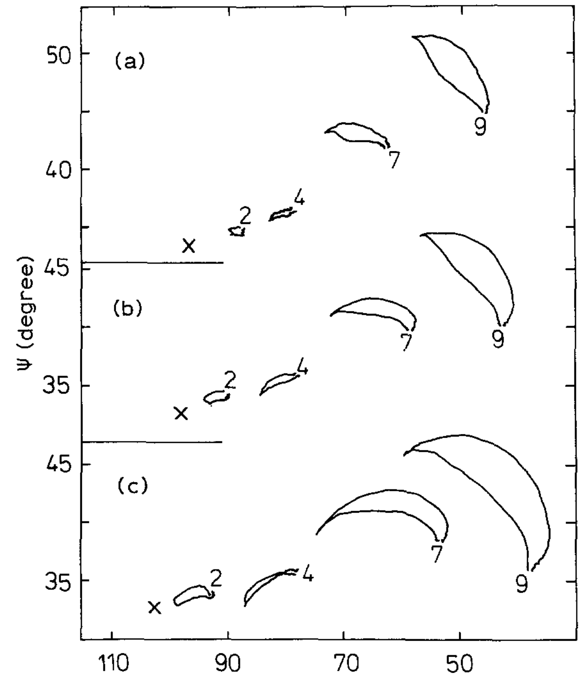


Fig. 5. Δ/Ψ plot for wavelengths 400 nm (a), 450 nm (b) and 500 nm (c).

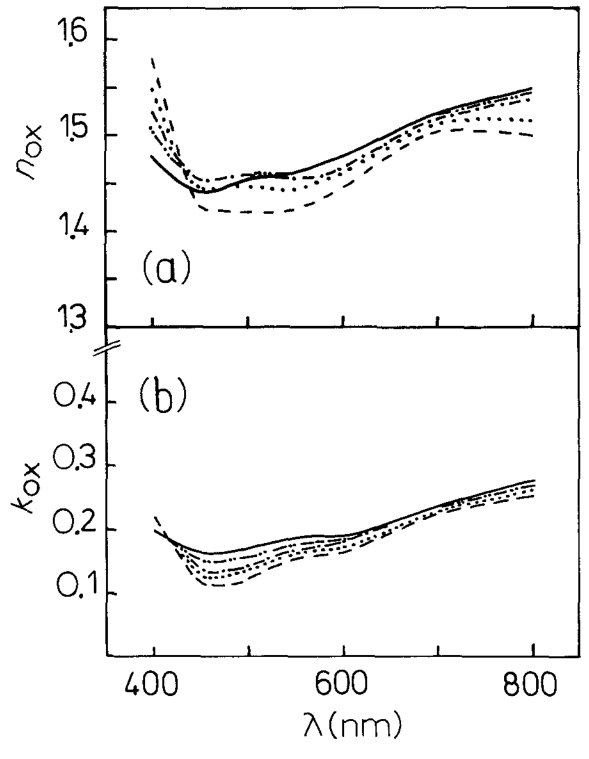


Fig. 6. (a) Refraction index of the oxidized film, n_{ox}, as function of wavelength. (b) Absorption coefficient of the oxidized film, k_{ox}, as function of wavelength; plotted are the connecting lines (interpolations) between the experimental values at 400, 450, 500, 550, 600, 700 and 800 nm. (– – –) 1st, (······) 3rd, (–·–·–) 5th, (–··–) 7th, (———) 9th cycle.

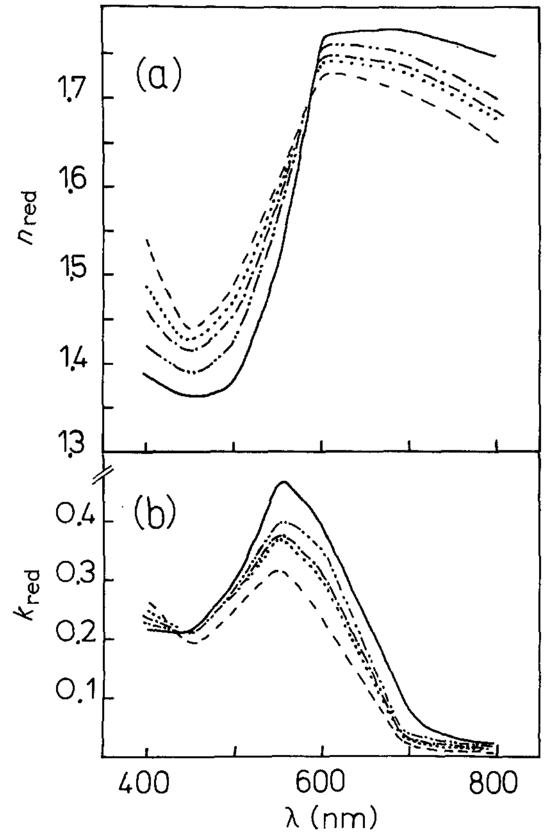


Fig. 7. (a) Refraction index n of the reduced film, n_{red}, as function of wavelength. (b) Absorption coefficient of the reduced film, k_{red}, as function of wavelength; plotted are the connecting lines (interpolations) between the experimental values at 400, 450, 500, 550, 600, 700 and 800 nm. Different cycles, see Fig. 6.

experimental points for fewer layers in the fitting procedure; for instance, only the points measured for the oxidation cycles n, $n + 1$ and $n + 2$. In this case, the dependence of the optical parameters on the thickness can be determined. The n and k values for the oxidized film are shown in Fig. 11, the n and k values for the reduced film are shown in Fig. 12, in each case for 3 thickness values.

Comparing the optical constants of the film formed at low overpotential with the optical constants of the film formed at high overpotential, a decrease of n by approx. 0.1 and a decrease of k by approx. 0.3 is observed and the absorption band of the reduced film has disappeared.

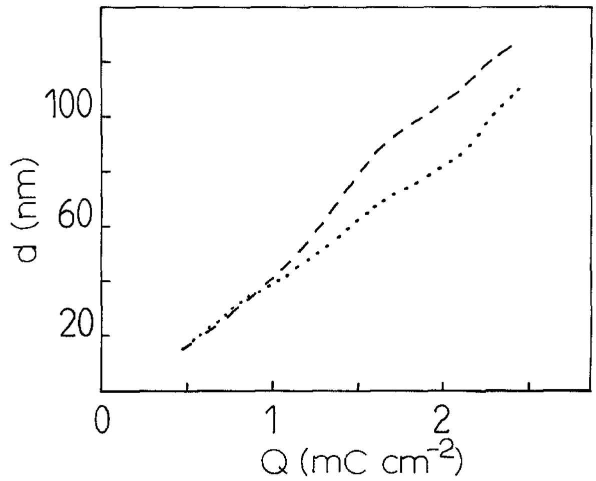


Fig. 8. Optical thickness, d, against electrical charge, Q, determined from integration of the cathodic current for reduction of the film; oxidized film (······), reduced film (— — —).

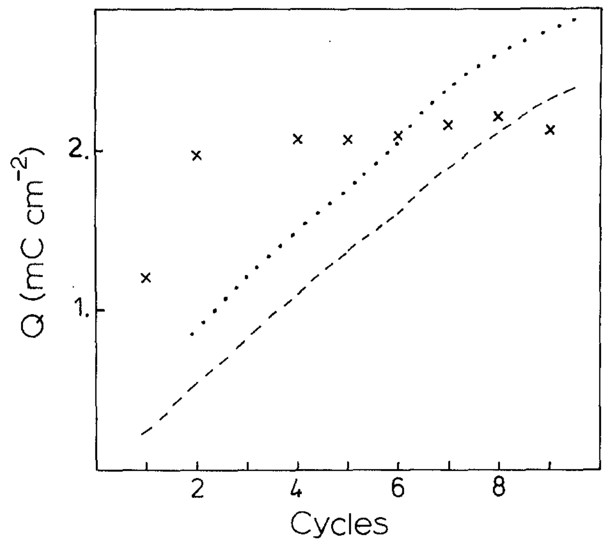


Fig. 9. Change of charge with the number of cycles during film formation (×), oxidation (······), and reduction (— — —) of the film, respectively.

The ellipsometrically determined thickness versus the charge from the reduction cycle is shown in Fig. 13. Comparing this film with the film formed at high overpotential, a larger thickness at similar Coulomb values is observed. From Fig. 13, a charge/thickness ratio of 12.2 μC nm^{-1} results, while in the case of

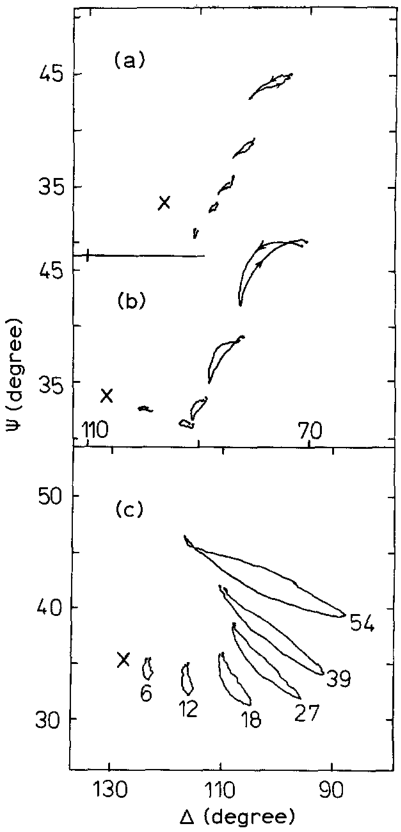


Fig. 10. Δ/Ψ plot for a potential-time program, similar to Fig. 2b but with an increased oxidation potential of 922 V (915 mV in Fig. 2b); at this potential slow film growth occurs.

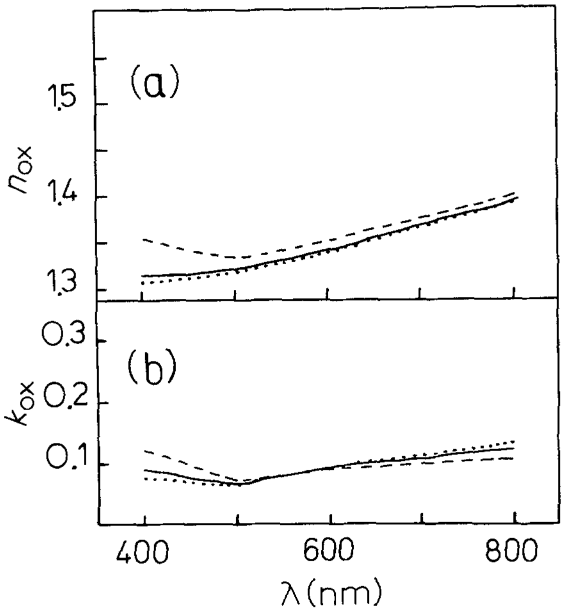


Fig. 11. Refraction indices, n_{ox}, and absorption coefficients, k_{ox}, as function of wavelength for the oxidized film, $d = 90\,nm$ (– – –), 120 nm (———), 170 nm (······).

Fig. 8 the ratio was $19.7\,\mu C\,nm^{-1}$. Furthermore, the thickness of the oxidized form of the film equals that of the reduced one. The charge, Q, against the number of cycles is shown in Fig. 14. The charge for oxidation is again higher than the charge for reduction, some charge is lost in the oxidation process.

The results show a remarkable difference between films formed under identical conditions but changing the overpotential from 65 to 7 mV. The decrease of the refraction index and the increased thickness for equal charge values give the impression of a film of less density for an overpotential of 7 mV compared with a film formed at an overpotential of 65 mV. This is somewhat surprising because an opposite effect had been expected from the theoretical arguments of a growth closer to the equilibrium.

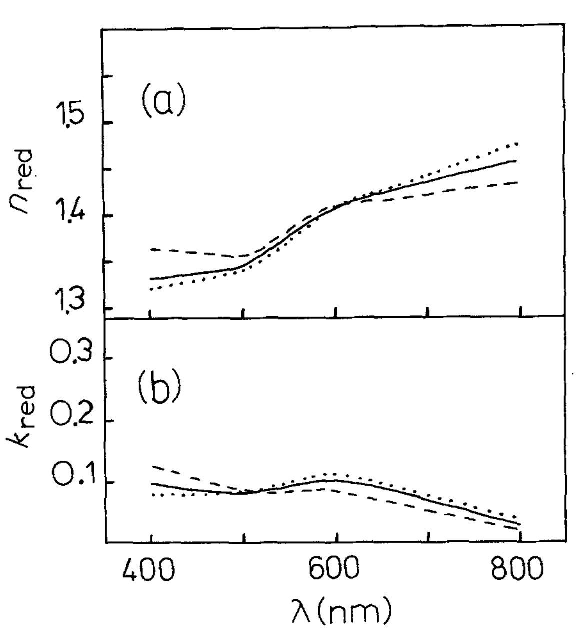


Fig. 12. Refraction indices, n_{red}, and absorption coefficients, k_{red}, as function of wavelength for the reduced film, $d = 90\,nm$ (– – –), 120 nm (———), 170 nm (······).

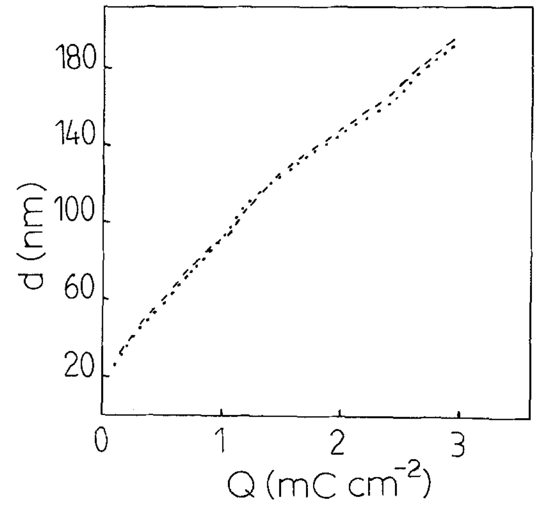


Fig. 13. Optical thickness, d, against Q. (······) oxidized film, (– – –) reduced film.

4. Discussion

4.1. *Absorption maximum*

For the homologous series of oligomeric 2,5-thiophenediylvinylenes and poly(2,5-thiophenediylvinylene), the energy values of the $\pi \rightarrow \pi^{*-}$ transition and the bond orders have been calculated, being in good agreement with the bond lengths estimated by X-ray diffraction patterns [4]. For an increasing number of vinylene units, n, the following maxima were calculated n/λ = 1/343, 2/412, 3/460, 4/490, 5/495, 7/510 nm and are in good agreement with the experimental data. The experimental value for the above mentioned polymer is 550 nm ([4], p. 2389).

In the present results the wavelength of the absorption maximum for k_{red} is 550 nm (see Fig. 7b). This peak agrees with the experimental data for poly(2,5-thiophenediylvinylene) in [4] indicating a high degree of conjugation. No absorption maximum for k_{ox} was

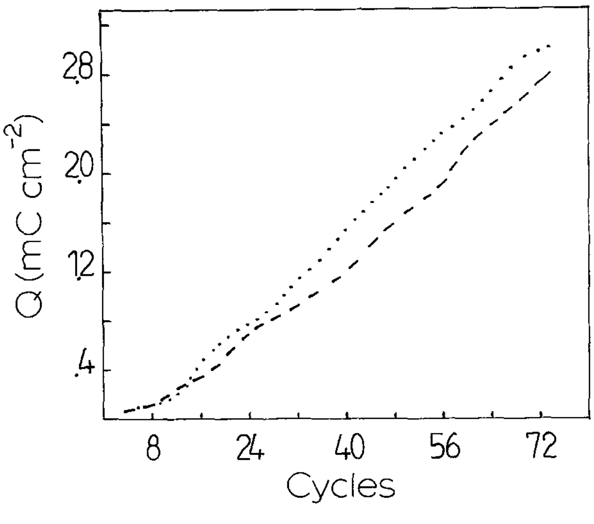
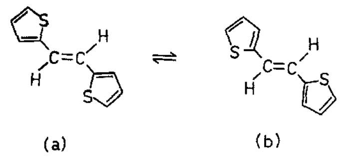


Fig. 14. Charge, Q, against the number of cycles. (······) oxidation, (– – –) reduction scan.

found in our investigation. Recently published spectrophotometric results on electrochemically formed poly(2,2′-bithiophene-5,5′ diyl) in its oxidized form show an absorption peak of 470 nm [5]. This absorption maximum would correspond to a conjugation of $n = 3$–4 in the series of the poly(2,5-thiophenediylvinylene)s.

4.2. *Structure*

The absorption spectrum of trans-1,2-di(2-thienyl)-ethylene (trans-DTE) shows a maximum at 345 nm, that of the cis form (cis-DTE) at 300 nm. FTIR spectroscopy of KBr pellets unequivocally demonstrated that the *trans* configuration of the double bond remained unaltered in the polymer [6]. The possible rotational isomers of trans-DTE [7] are:



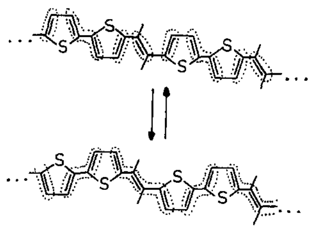
It is difficult to decide whether the S-cis–cis form (a) or the S-trans–trans form (b) is present in the solution; the S-cis–cis form (a), however, is tentatively preferred [7]. In the solid state the form (a) has been found by X-ray studies [8].

4.3. *Doping*

A linear relation exists between ellipsometric thickness d and charge Q. The thickness decreases by doping. For films with the thickness of about 90 nm the change was of the order of 26%. For polymers made from 3-methylthiophene [9] and thiophene [2], the opposite effect was observed. Measurements on poly(2-aminophenol) electrochemically formed in aqueous solution also show a larger thickness for the doped state than for the reduced form [10].

Coulometric measurements (2.5 electrons per starting molecule of DTE) associated with high yields of electrosynthesis strongly support the trans-structure [4] for the vinylene units in the polymeric chain besides neutral and about 50 mol % of charged bithienyl units according to the given formula (section 1).

The decrease of the film thickness during doping (accompanied by the uptake of ClO_4^- anions) may be explained by a concerted change of the S-trans-trans to the S-cis–cis structure (or reverse) during the loss of an electron to the charged form of the bithienyl units in the polymeric chain. For this structural consideration it is thought that there are only bithienyl units with the two sulphur atoms i opposite positions because of the dipolar character of the electronegative sulphur atoms. When the charge to oxidize or reduce the film, Q, approaches zero, the ellipsometric value of d is still 20 nm. This may be interpreted by a two-layer model with a film of 20 nm on the electrode surface oxidized or reduced by only a small amount of charge and a thicker electroactive film on top. This complication was not taken into account in the data evaluation procedure; the ellipsometric data were calculated assuming an isotropic and homogeneous film. The optical parameters n, k and d determined for this early state of growth would then represent average values between the two films.



4.4. *Small overpotential*

Growth at 922 mV led to the formation of less compact films. In the investigated spectral region no absorption maximum is observed. It is suggested that this may result from the small field strengths at the lower overpotential.

Acknowledgement

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