Highly anisotropic electrically conducting films based on polypyrrole*

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Electrically conducting films of polypyrrole prepared using a pulsed electrochemical potential exhibit a marked increase in molecular anisotropy, electrical conductivity and surface smoothness, as compared to equivalent films synthesized under constant potential conditions. These enhancements are only observed when the polypyrrole films are prepared from aqueous electrolytes containing toluene sulphonate as the dopant or counterion. X-ray scattering patterns show that the polypyrrole films are highly anisotropic with the planes of the pyrrole rings lying preferentially parallel to the electrode surface. The pulse lengths and voltages are most important to preparing enhanced films and appear to indicate that these improved films grow as a consequence of an increase in the number of equivalent growth sites.

(Keywords: polypyrrole; molecular anisotropy; electrical conductivity)

INTRODUCTION

Polymers are intrinsically anisotropic at a molecular level. It is clear that in many areas of polymer science there is much to be gained from translating that molecular anisotropy to the macroscopic scale. Electrically conducting polymers are no exception, and for both polyacetylene[1] and polyaniline[2] it has been elegantly demonstrated that the introduction of high levels of global molecular anisotropy has a marked impact upon the optical and electrical properties. Of course a basic problem with many highly conjugated polymers is that they are intractable, and hence it proves impossible to perform reorganizational operations after preparation. For this reason, precursor routes for polyacetylene and other polymers have been developed which allow molecular anisotropy to be developed during film preparation[1]. In general this anisotropy is associated with the preferential alignment of the long axes of substantial segments of polymer chains. We have shown, using both X-ray and neutron scattering techniques[3–8], that under certain conditions films prepared from pyrrole with aromatic dopants exhibit an anisotropic molecular organization in which the planes of the pyrrole and dopant units lie preferentially parallel to the electrode surface. In the general area of electrodeposition the generation of highly ordered materials is not uncommon; consider, for example, the production of metals or organic superconductors. The extensive literature on polypyrrole highlights the wide variety of electrochemical parameters that can be varied, and many examples are provided in recent reviews[9–11]. Each of these electrochemical parameters, such as electrolyte, temperature and electrode material, has some impact upon the resultant film and its properties. It is therefore appropriate to ask why such organized structures as observed for other materials, are not observed with polymeric conductors and if there are particular preparation conditions which would allow the electrochemical synthesis of crystalline polypyrrole. For example, is it the case that polypyrrole normally consists of microcrystallites which are randomly oriented due to a rough and ill-defined growth front? A practice employed in electroplating to provide well-defined growth fronts, is the utilization of a pulsed electrochemical potential rather than steady galvanostatic or potentiostatic conditions. Surprisingly there is little in the literature on the application of these procedures to conducting polymers[12]. This paper focuses on the employment of pulsed potentials for the electrochemical polymerization of polypyrrole based films. The influence of the pulse potential variables on the resultant films is examined in terms of growth rate, surface profile and molecular anisotropy. It will be demonstrated that the use of particular pulse structures leads to the growth of films with high levels of preferential alignment of the pyrrole rings with respect to the electrode surface. These results impinge on a general understanding of electrochemical growth processes.

EXPERIMENTAL

Materials

All of the polymer films were prepared from pyrrole which had been distilled under reduced pressure. The electrolyte was prepared from deionized water and sodium *p*-toluene sulphonate. In addition, some preliminary syntheses were performed using other sodium based salts; each was used as supplied by Aldrich. The electrochemical polymerizations were performed using a standard solution of 0.2 mol pyrrole and 0.1 mol of the appropriate salt in deionized water.

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Electrochemistry

The electrochemical polymerization reactions were performed using a three-compartment cell in conjunction with a Sycopel potentiostat operated with a computer interface using a software package ECOS for control and data handling[13]. The complete electrochemical cell was immersed in a temperature controlled bath with a temperature range of -40 to 40°C. A coated glass electrode (Baltracon Z10, $\sim 20\,\mathrm{mm} \times 40\,\mathrm{mm}$) was used as the working electrode and a carbon rod as the secondary electrode. All potentials were measured with respect to the saturated calomel electrode (SCE). Two types of electrochemical procedures were employed. The first involved the use of a constant potential with respect to the reference electrode as is generally employed in electrochemical growth. For this the current passed through the cell was recorded in the computer system and integrated to allow films to be prepared on a constant charge passed basis. Typically the total charge passed was 16 C. The second procedure employed was a pulse mode in which an oxidizing voltage V_o was applied for t_o seconds, followed by the application of a reducing voltage V_r which was applied for t_r seconds. In general $V_o = 1.2\,\mathrm{V}$ (*versus* SCE) and $V_r = 0\,\mathrm{V}$ (*versus* SCE). The other variables of the pulse train, namely t_o and t_r, could be varied independently from 0.1 to 100 s. The current response was recorded using a digital storage oscilloscope as a function of time. In this mode a specified number of pulses was applied to the cell for each film preparation; for example, with $t_o = t_r = 1\,\mathrm{s}$, 10000 pulses gave a free-standing film of $\sim 10\,\mu\mathrm{m}$. The films prepared by either procedure were removed from the glass substrate, washed in water/acetonitrile and dried under reduced pressure at room temperature.

X-ray scattering

X-ray scattering intensity data were recorded using a diffractometer operating in a symmetrical mode, which allowed a fixed angular relationship (χ) between the plane of the sample and the scattering vector **s**, where $|s| = 4\pi \sin\theta/\lambda$, to be maintained over the complete scattering vector range considered[5,14]. When $\chi = 0°$ this gives an arrangement in which the scattering vector lies within the plane of the sample and hence probes the structure in that plane: when $\chi = 90°$ the scattering vector is normal to the plane of the sample and hence probes the structure through the thickness of the film. The diffractometer was equipped with a copper target X-ray source, an incident beam monochromator and pinhole collimation. Samples for X-ray scattering measurements were prepared by cutting the polymer film into narrow sections of the order of 2 × 4 mm, and these were stacked on top of each other preserving the relative orientations. Using these procedures quantitative intensity data could be recorded over the scattering vector range $s = 0.2$–$6.2\,\text{Å}^{-1}$. The data displayed below are as measured and are not corrected for experimental factors such as polarization and absorption. For the thin films considered here the latter is not a significant factor.

Electrical conductivity

Electrical conductivity measurements were made using a standard four-probe technique at room temperature in air. The probes were placed on the growth surface of the film.

Surface profile

The nature of the surface morphology of the growth face was examined using a Philips scanning electron microscope SEM515 after coating with gold. A quantitative measure of the surface profile was obtained using a Taylor Hobson TalyStep which operates through measuring the displacement of a contact stylus. This system provided a sensitivity in terms of surface displacement of 0.4–0.001 μm and a spatial resolution of 0.002 μm.

RESULTS

The first series of electrochemical polymerizations of polypyrrole/toluene sulphonate employing the pulsed mode were made with $V_o = 1.2\,\mathrm{V}$ and $V_r = 0\,\mathrm{V}$ and by systematically varying $t_o = t_r$ from 0.2 to 100 s. *Figure 1* shows the current–time curves for pulse times of $t_o = t_r = 1$, 10 and 30 s. These have a common form in that accompanying the application of V_o there is a rapid increase in current which then decays slightly to a steady state value after $\sim$0.5–1 s. Of course, for short pulse times (t_0) this steady state is not reached. There appears to be no systematic change in the decay rate or the value of the steady state current as $t_o = t_r$ is varied. The change of voltage from V_o to V_r is also accompanied by a rapid change in the sign of the current. There is a decay in the magnitude of the current from the instantaneous value which has an effective correlation time of $\sim$50 s. Again, the principal difference between the differing pulse times is the extent to which the current decays rather than the decay rate.

The mass of polypyrrole/toluene sulphonate deposited per pulse is almost linear with pulse length. Such values for the mass deposited per pulse are average values taken from films prepared using a number of pulses (20 to 500 depending upon the values of t_o and t_r). Test experiments performed using a much larger number of pulses gave similar values for the mass deposited per pulse indicating that the deposition rate was reasonably uniform with time. *Figure 2* shows a plot of the mass deposited for a series of samples prepared with almost equivalent thicknesses but with varying values for $t_o = t_r$. A power law fit to this data gives an exponent of 1.2 with a correlation coefficient of 0.99. The greatest deviation from linearity is at small pulse times. This effect is shown more clearly in *Figure 3* where the mass per pulse per second is plotted against the reciprocal of the pulse length t_0 for a fixed value of t_r. The constant growth rate at large pulse times contrasts with the rapidly reducing growth rate at smaller pulse lengths.

The films prepared using the pulsed mode of electrochemical polymerization are noticeably smoother on a macroscopic scale as may be seen from their reflectivity. *Figure 4* shows the surface morphology for a film prepared using the pulse mode with $t_o = t_r = 1$ s compared with that observed for a film prepared using a constant electrochemical potential. The pulse mode film exhibits a smoother growth face, and the surface irregularities are less in number. This may be seen more clearly in a measurement of the surface profile using a Talystep system as shown in *Figure 5*. The film prepared using a constant potential has a highly irregular surface with an average amplitude for the surface roughness of $\sim 1\,\mu$m. In contrast, the film prepared using the pulse mode is flat with an undulating surface of $\sim 0.1\,\mu$m in amplitude

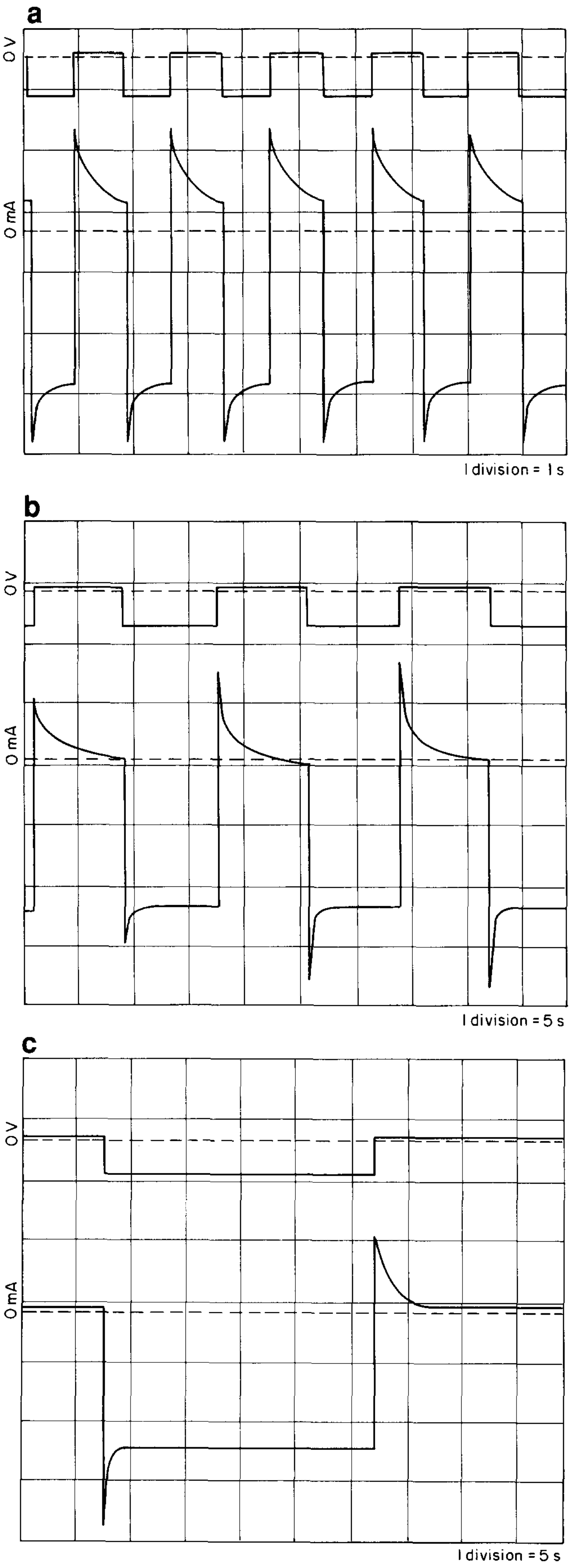

Figure 1 Plots of the current recorded during the electrochemical synthesis of polypyrrole in an aqueous electrolyte with sodium *p*-toluene sulphonate, as a function of time for three different pulse sequences with $V_o = 1.2$ V and $V_r = 0.0$ V (*versus* SCE): (a) $t_o = t_r = 1$ s; (b) $t_o = t_r = 10$ s; (c) $t_o = t_r = 30$ s. The top curve in each case shows the electrochemical potential applied, while the lower curve is the resultant current. For this latter curve the vertical scale is 1 division = 2 mA

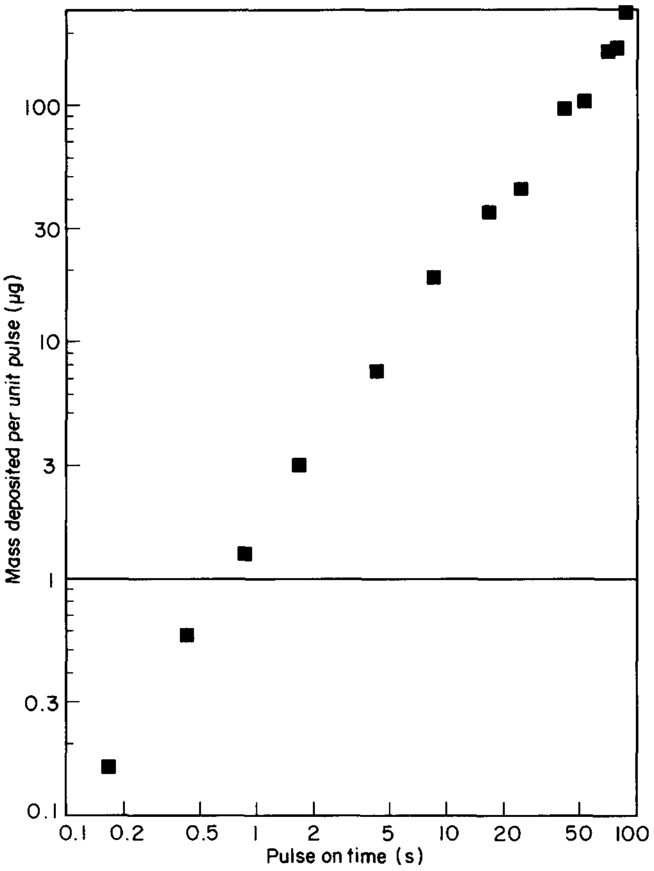

Figure 2 Mass deposited per pulse plotted as a function of the pulse length for an electrochemical synthesis of polypyrrole with *p*-toluene sulphonate as the dopant, $t_o = t_r$ and $V_o = 1.2$ V and $V_r = 0.0$ V (*versus* SCE)

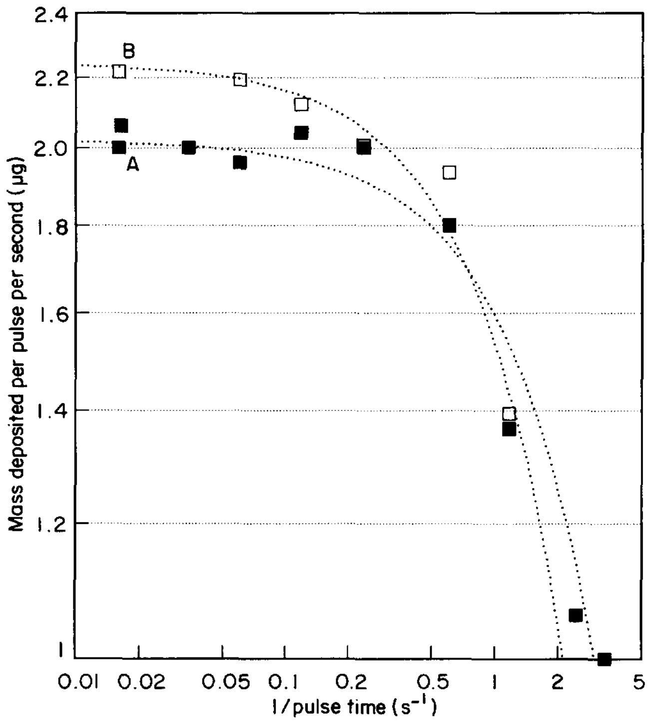

Figure 3 Mass deposited per pulse normalized to the pulse length plotted as a function of the reciprocal pulse length for an electrochemical synthesis of polypyrrole with *p*-toluene sulphonate as the dopant and $V_o = 1.2$ V and $V_r = 0.0$ V (*versus* SCE) with (A) $t_r = 1$ s and (B) $t_r = 2$ s

with additional sharp growth features with a low number density. In fact the surface profiles shown in *Figure 5* were obtained from films which were much thinner than normal. This was necessary since 'normal' films prepared using a constant potential were too rough to evaluate, that is, the amplitude variation was >4 µm. In contrast, films prepared using the pulsed potential show only a marginal increase in roughening with thicker films. *Figure 6* shows quantitatively how the surface roughness varies as a function of the pulse step time. There is a marked increase in the surface roughness when the pulse time exceeds a few seconds. The surface roughness for films prepared using short pulse times is substantially smaller than for that prepared by the use of a constant potential.

It is noticeable that increasing $t_0 > t_r$ as well as increasing t_0 results in rougher films. In contrast, increasing t_r has little impact on the surface morphology unless the t_r is greatly increased over t_0. We have reported in detail the results using the pulse mode with $V_0 = 1.2$ V and $V_r = 0$ V. For a pulse train with $t_0 = t_r = 1$ s increasing $V_0 > 1.2$ V has the effect of producing films with a rougher surface, lower conductivity and less molecular anisotropy. This mirrors observations made on polypyrrole films prepared using a constant potential[4]. For V_0 in the range 0.8–1.2 V the resulting films are rather similar. If the level of V_r is increased this results in poorer quality films. It is striking that under similar conditions to those reported above, polypyrrole films grown from acetonitrile or propylene carbonate do not exhibit high quality properties when prepared using the pulse mode. Films prepared from aqueous solution initially by the pulse mode revert to a rougher growth surface if growth is continued with a constant electrochemical potential as shown in *Figure 5b*.

The structure of the pulsed electrochemical potential has a significant impact upon the electrical conductivity of the resultant films. *Figure 7* shows the measured conductivity for a series of films plotted as a function of the variation in pulse length with $t_0 = t_r$. There is a doubling of the resultant electrical conductivity in moving from constant potential preparation to the pulse mode. The peak value of the conductivity was obtained for films prepared with a pulse length of 1 s. Decreasing the pulse length resulted in a slight but significant reduction in the electrical conductivity. The variations with pulse length observed are typical of several series

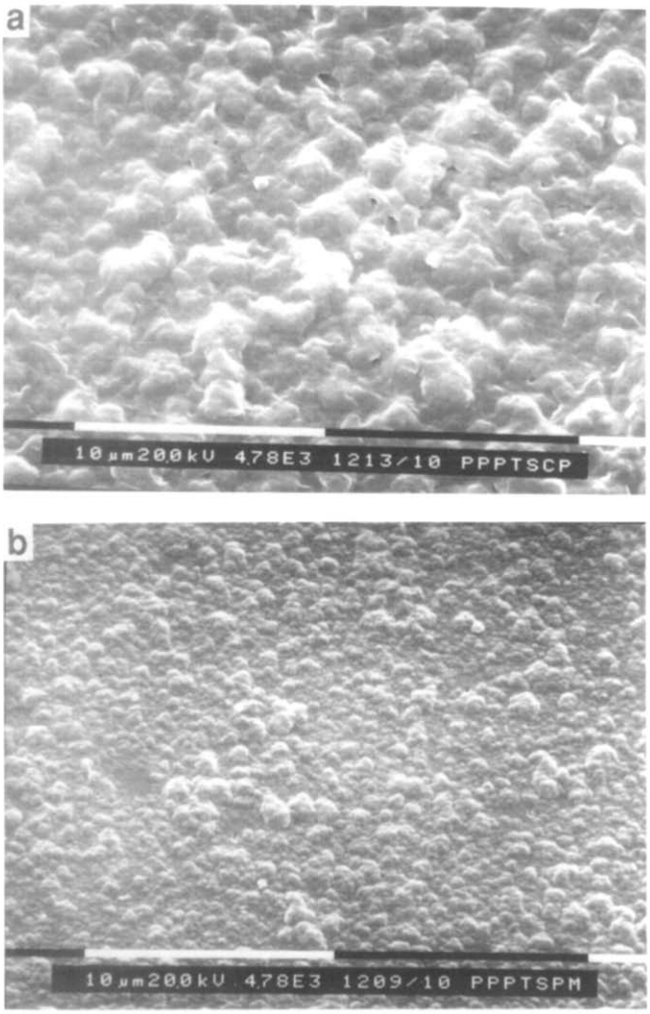

Figure 4 SEM micrographs of the growth faces of polypyrrole films prepared with *p*-toluene sulphonate as the dopant using equivalent conditions with (a) constant potential of 1.2 V (*versus* SCE) and (b) pulsed potential $V_0 = 1.2$ V and $V_r = 0.0$ V (*versus* SCE) and $t_0 = t_r = 1$ s

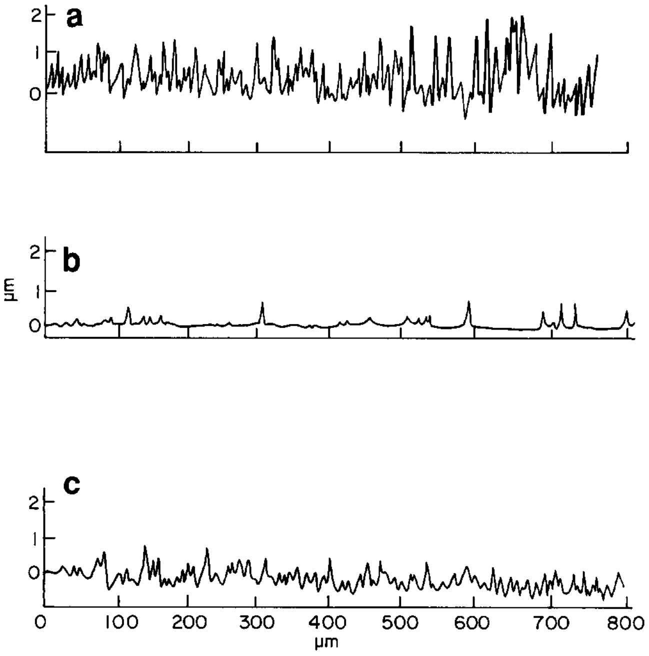

Figure 5 Profiles of the growth faces of polypyrrole films prepared with toluene sulphonate as the dopant using (a) constant potential, (b) pulsed potential and (c) pulsed potential for 50% of the growth time followed by the application of a constant potential

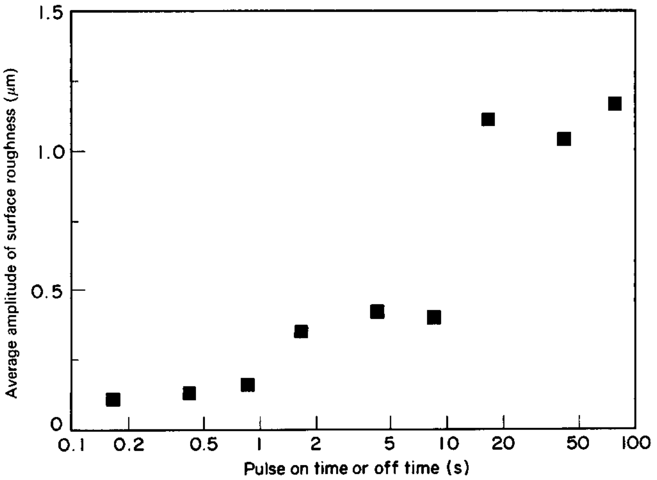

Figure 6 Plot of the average amplitude of surface roughness against the pulse length for films

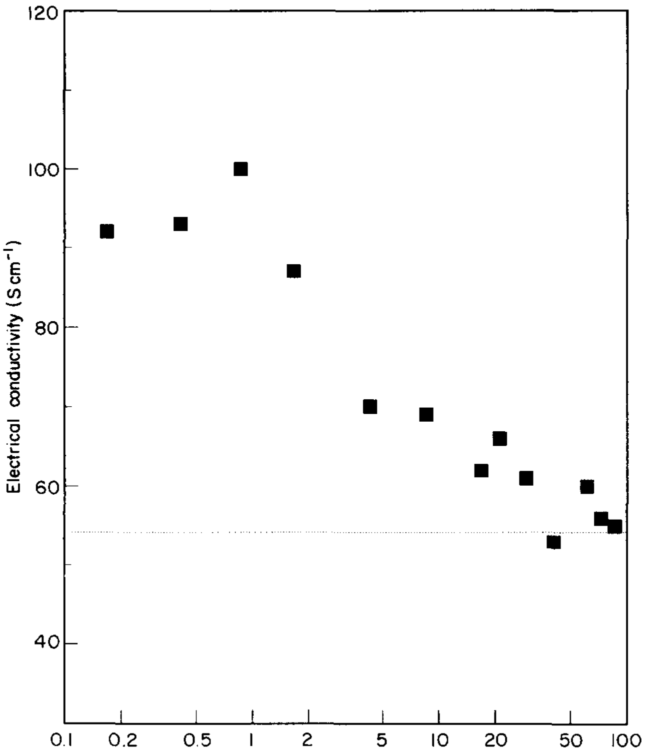

Figure 7 Electrical conductivity against pulse length for polypyrrole films prepared with *p*-toluene sulphonate, using pulse sequences with $V_o=1.2$ V and $V_r=0.0$ V (*versus* SCE) and $t_o=t_r$. The broken line represents the value obtained for films prepared under equivalent constant potential procedures

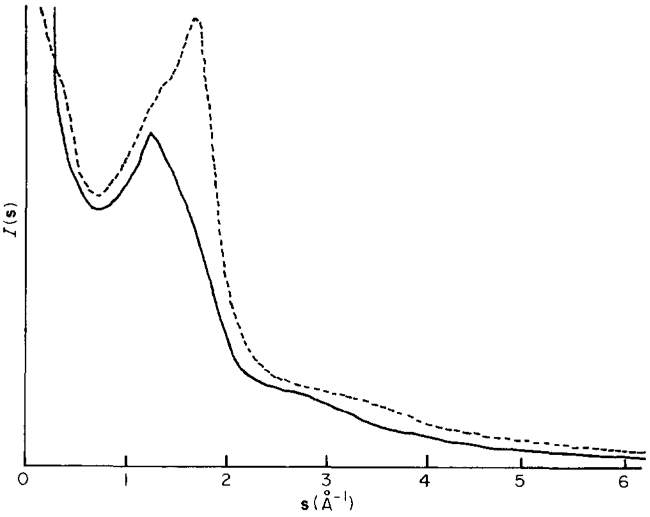

Figure 8 Scattered X-ray intensity $I(\mathrm{s})$ from a sample of polypyrrole prepared using a constant electrochemical potential recorded for two settings of $\chi=0$ (——) and 90° (– – –)

of samples. The variation in properties for samples prepared using the same condition was <5%.

The use of the pulse mode also has marked impact upon the nature of the molecular organization in films prepared in that manner. *Figure 8* shows the X-ray scattering curves recorded for a sample of polypyrrole/toluene sulphonate prepared using a constant electrochemical potential. The curves shown are for the arrangements with $\chi=0$ and 90°. Both curves exhibit broad peaks indicative of a highly disordered structure. The fact that the peaks in the two curves are not at the same scattering vectors indicates directly that the material is anisotropic at both a local and global scale. The peak at $\mathrm{s}\sim1.7$ Å^{-1} may be related to the correlations between layers of aromatic rings[5]. The fact that this is most intense for the curve recorded with $\chi=90°$ means that those aromatic planes are preferentially aligned with respect to the electrode surface. The level of the anisotropy is reflected in both the difference between the positions of the diffuse maxima and the relative intensities in the two curves at the same scattering vector values. Although the anisotropy displayed in *Figure 8* is significant, it is far from that expected for a crystal. *Figure 9* shows the equivalent scattering curves for a polypyrrole film prepared using the pulse mode of electrochemical growth. The substantial improvement in the level of global anisotropy is immediately obvious. The peak at $\mathrm{s}\sim1.7$ Å^{-1} for the curve with $\chi=90°$ is sharper and much more distinct than for the equivalent data for the constant potential sample. Importantly the intensity at $\mathrm{s}=1.7$ Å^{-1} with $\chi=0°$ is very low indicating a high level of anisotropy. In *Figure 10* the normalized ratio of the intensities at $\mathrm{s}=1.7$ Å^{-1} for the two scattering curves is plotted as a function of the pulse step time used in the film preparation. This intensity ratio provides one measure of the level of anisotropy and there is a clear trend which mirrors that for surface roughness (*Figure 6*) and electrical conductivity (*Figure 7*). However, the anisotropy appears to drop with increasing pulse length time in two distinct stages. The first corresponds to ~25% of the total drop and occurs over short pulse lengths of a few seconds. This parallels the drop in conductivity and surface roughness. There is a further large drop when the pulse length is increased substantially. As with the electrical conductivity plot there is a small drop in anisotropy for films prepared with a pulse length of <1 s.

The positions of the two prominent peaks for the two curves ($\chi=0$ and 90°) remain essentially unchanged with varying pulse length, although there is a marked change in the intensity ratio. This indicates that although there is a significant increase in the level of global anisotropy, the underlying local structure remains largely unchanged. *Figure 11* shows a plot of the X-ray scattering intensity

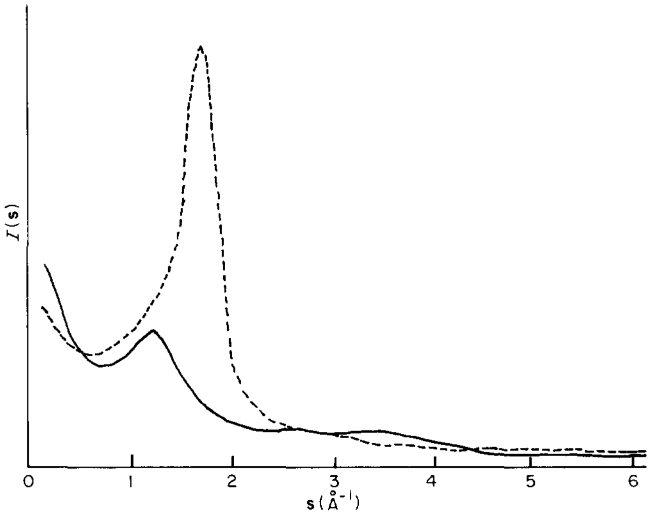

Figure 9 Scattered X-ray intensity $I(\mathrm{s})$ from a sample of polypyrrole prepared using a pulsed electrochemical potential, recorded for two settings of $\chi=0$ (——) and 90° (– – –)

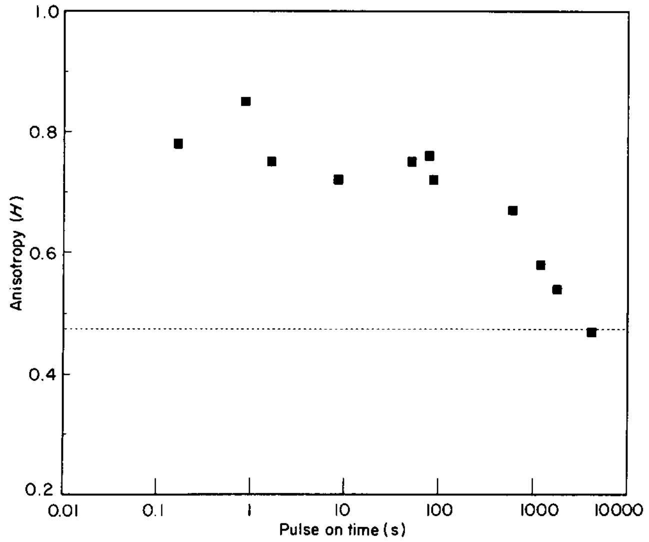

Figure 10 Plot of the anisotropy H measured from the X-ray scattering curves of the series of samples shown in *Figure 2*. $H=[I_{90}(s)-I_0(s)]/I_{90}(s)$ with $s=1.7\,\text{Å}^{-1}$; this provides a measure of the global anisotropy of the planes of the aromatic groups. The broken line represents the value obtained for films prepared under equivalent constant potential procedures

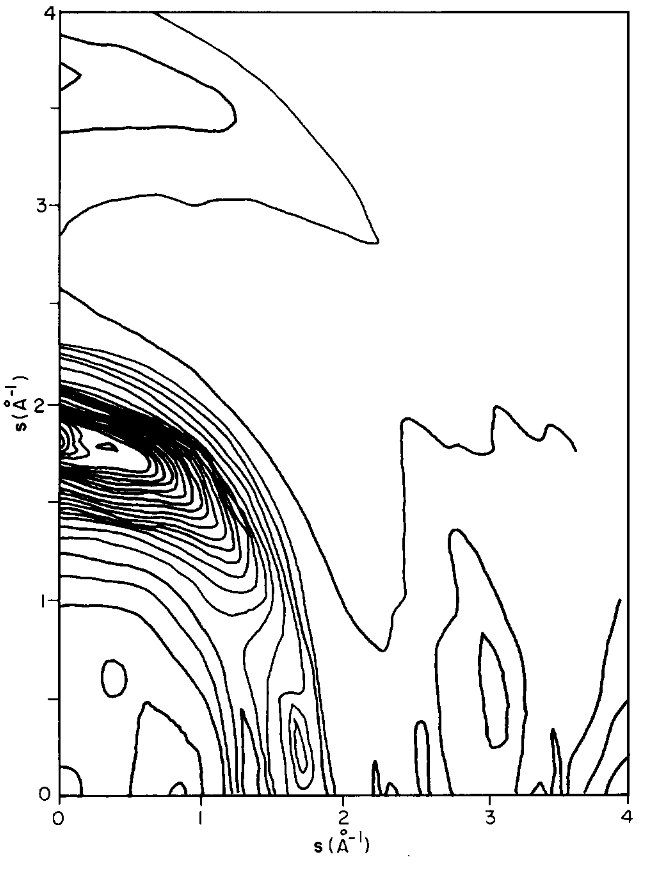

Figure 11 Scattered X-ray intensity $I(s, \chi)$ for a sample of polypyrrole prepared using a pulsed electrochemical potential. The vertical axis of the plot corresponds to $\chi=90°$, that is, structural correlations normal to the electrode surface

function $I(s, \chi)$ for a polypyrrole film grown from aqueous solution using the pulse mode. The marked arcing shows clearly the high level of preferential molecular alignment. The breadths of the peaks in terms of Δs provide information about the spatial extent of the correlations. For the peak at $s \sim 1.7\,\text{Å}^{-1}$, $\Delta s=0.3\,\text{Å}^{-1}$ giving a coherence length of 21 Å. This is comparable to that displayed by many crystalline polymers with low levels of crystallinity or disordered structures[15].

These figures show that polypyrrole films prepared with toluene sulphonate using the pulse mode exhibit a markedly smoother growth face, higher conductivity and substantially enhanced anisotropy. In contrast it was found that films prepared using non-aromatic based dopants such as BF_4^- showed very little change in appearance or conductivity when a pulsed potential was employed rather than a constant potential. None of these films exhibited any trace of macroscopic anisotropy. The current–time curves obtained for these 'spherical' dopants were basically similar to those observed for polypyrrole/toluene sulphonate. However, it was noticeable that the 'undoping' current decayed more slowly for the spherical counterions compared to aromatic based dopants. For films prepared with BF_4^- or SO_4^- the growth rate with changing pulse length was linear. This compares with power law relationships found for the polypyrrole/toluene sulphonate system with an exponent of ~ 1.2 and for polypyrrole/naphthalene disulphonate an exponent of ~ 1.3. The behaviour of the polypyrrole/naphthalene disulphonate system was very similar to that described above for the films prepared using toluene sulphonate.

DISCUSSION

It is clear that the use of the pulse mode results in increases to the resultant electrical conductivity, the level of molecular anisotropy and decreases the roughness of the growth surface. This is only significant in the time–voltage regime examined when the solvent is water and the dopant is *p*-toluene sulphonate. We shall consider first the effect of the preparation procedure on the nature of the growth front. Growth can only take place on a conducting surface. Initially the electrode surface is clear and uniform, although doubtless there are some variations in the potential due to the geometry of the cell. Growth initiates at a limited number of sites. In the pulse mode the material at these sites is reduced in the reduction pulse and hence its electrical conductivity is much decreased. The extent of reduction will depend upon the values of V_r and t_r. Reapplication of the oxidizing potential, will cause redoping for the initial growth sites. The time taken for this redoping will depend upon the value of V_o. We can broadly associate this time with the initial decay in the current accompanying the oxidizing pulse. Typically this is $\sim$0.5–1 s as may be seen from *Figure 1*. During that time, growth on the initial sites on the electrode is frustrated and hence nucleation at other positions on the electrode is more probable. As a result, there is a large number of equivalent nucleation and growth sites. This hypothesis was confirmed by optical microscopy in which the initial number of nucleation sites for the pulse mode was much greater than that observed for the constant potential procedure for electrochemical growth. In other words, the effect of pulsing is largely to make all points on the electrode surface more equivalent. A large number of equivalent sites leads to a smoother growth front. The degree of equivalence will depend upon the extent of the undoping during reduction and the speed of redoping. Clearly if the oxidation pulse length is large, then growth will occur also on the initial sites. Since there is a greater concentration of equipotential lines due to the curvature of the growth front, growth will be more rapid. This effect is self propagating in that once the surface roughness has developed its curvature acts to maintain the disparity of growth rate. The objective must be to maintain the equivalence of all sites on the electrode. This is achieved by keeping $t_o \sim \Delta t_d$, where Δt_d is the time for redoping. For a particular value of t_r, for example 1 s, there will be an optimum oxidizing voltage V_o. Increasing the voltage above that level will decrease Δt_d and hence the surface will roughen. This is exactly what is observed. Decreasing the voltage below the optimum value will reduce the overall growth rate but will maintain a uniform growth face. Although the mechanism has been considered with respect to a clean electrode surface, a similar mechanism occurs throughout the film growth. Material which has been recently deposited is more likely to represent a potential surface roughening point. On the other hand this material will be more easily undoped and hence growth in the following pulse is inhibited. This level of inhibition is determined by the relative values of t_r and t_o in addition to the absolute value of t_o. It is noticeable that the rate of undoping is much faster for toluene sulphonate compared with BF_4^-. We attribute this to the difference in the extent of undoping. In the case for which toluene sulphonate is the dopant, we conclude that only the dopants near to the growth surface are extracted. For other dopants, especially BF_4^-, the long undoping time is related to the fact that dopants from throughout the sample are removed.

Such a model provides a mechanism for smooth growth but does not explain the preferential alignment of the aromatic planes parallel to the electrode surface as shown by the X-ray scattering experiments. A polypyrrole molecule is planar unless particular defects are introduced[16]. This has been demonstrated in the case of copolymers of pyrrole and *N*-methyl pyrrole since the global anisotropy is lost when significant levels of *N*-methyl pyrrole are introduced into the chain[17]. The bulky substituents on the *N*-methyl pyrrole cause the units to twist out of planarity. Whether deposition occurs in terms of whole polymer molecules or by sequential addition of monomers the natural alignment of the pyrrole units would be parallel to the surface. This is doubtless encouraged by the use of planar types of dopant as established in an earlier study[5]. The larger aromatic dopants are necessary to give a fully intercalated structure. The use of 'spherical' counterions such as BF_4^- leads to a disruption of the layered structure on space filling grounds[5]. An alternative view point would be that the polymer chain grows with a helical conformation with the helix axis normal to the electrode surface as postulated from some preliminary scanning tunnelling microscopy studies[18]. This would also be compatible with the main features of the X-ray scattering data although there is little evidence from the higher scattering vector data for the regularity required for a helical structure.

The level of preferential alignment of the aromatic rings to the electrode surface increases if the pulse mode of electrochemical growth is employed. The level of macroscopic anisotropy is dependent upon both the global morphology and the local structure. For a rough growth face the pyrrole rings would be distributed with a range of orientations with respect to the electrode surface and hence a high global orientation could not be achieved. The X-ray scattering patterns show that there are additional factors which relate to the global level but which result from improvements to the local structure and packing. This may be seen from the widths of the scattering maxima by comparing *Figures 8* and *9*. These improvements to the local packing may arise from less defective chains and/or better assembly during growth. High levels of global molecular anisotropy require both a smooth growth front and local anisotropic deposition or growth. It would seem reasonable to relate the two stages of the loss of substantial anisotropy by increasing the pulse length as shown in *Figure 10* to these two requirements.

It is appropriate to question why a crystalline material does not result as is the case for metals and some other organic materials. For metals it is thought that surface diffusion of ions with their solvation shells removed or displaced plays a controlling step in the crystallization processes. If complete or partially formed polypyrrole molecules deposit on the electrode, surface diffusion would be extremely limited. Moreover the basic building blocks are then non-equivalent due to the widely differing chain configurations and hence would be non-crystallizable. If pyrrole rings attach sequentially to the growth front the situation is less clear. At low current densities when surface diffusion would be the limiting step there are specific sites on the growth front in a similar manner to a crystalline film of metal or low molar mass compound. It is possible that the overriding interaction is for preferential alignment rather than specific spatial correlations. The chemical energy of polymerization is high compared with any potential crystal field and this may encourage a more random deposition structure.

A differing view of the pulse mode of electrochemical deposition is that it slows down the growth rate as shown in *Figure 3*. It has been reported several times that preparation at lower temperatures can lead to films with enhanced electrical conductivity[4,19–21]. These procedures may have a common advantage in that a lower growth rate will lead to more growth sites and hence a more uniform growth face. This would suggest that surface diffusion is a significant stage in the electrochemical growth of polypyrrole.

CONCLUSIONS

1. The use of a pulsed electrochemical potential for the preparation of electrically conducting films of polypyrrole from aqueous electrolytes results in markedly smoother films compared with films prepared with a constant electrochemical potential.
2. Films prepared using a pulsed electrochemical potential are highly anisotropic for a restricted range of preparation conditions. The anisotropic X-ray scattering patterns reveal a more ordered structure with lateral correlation lengths of 21 Å.
3. These highly anisotropic films grown using a pulsed potential exhibit greater electrical conductivity.
4. Particular electrochemical conditions are important for the observation of these improvements. Such improvements are only observed with aqueous based electrolytes with aromatic based dopants. The pulse times and voltages are most important and appear to indicate that the improved films grow as a result of a high equivalence of growth sites which has been induced by the pulse sequence.

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