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Pentanol as co-surfactant in polypyrrole actuators

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

Conducting polymers have been investigated for the use as active component in polymer actuators. Addition of 1-pentanol as co-surfactant to the polymerisation solution is shown to increase the reversible linear strain that can be achieved with polypyrrole films doped with dodecyl benzene sulfonate (PPy–DBS). When such films are prepared without pentanol, the length change between the oxidised and the reduced state is 2.5%. If pentanol is added to the synthesis solution in concentrations above 2.4 vol%, a linear extension of 5.6% was measured at a constant load of 0.6 MPa. The morphology of the film is changed considerable upon pentanol addition, although electrochemical quartz crystal microbalance measurements indicate that pentanol is only incorporated in the polymer to a small extent. The mechanical properties, conductivity and doping level of PPy–DBS films show little or no changes with the addition of pentanol. The use of pentanol as co-surfactant during polymerisation will, therefore, be beneficial for the use of PPy–DBS as active component material in polymer actuators.

Keywords: Conducting polymer; Polypyrrole; Actuator

1. Introduction

Polymers with conjugated double bonds are distinguished from other types of polymers by their electronic conductivity and because they can be switched between two or more redox states having markedly different physical properties. These properties are the basis for a growing interest over the last two decades in the use of conjugated polymers as advanced functional materials. One of the most investigated material is polypyrrole (PPy), because of good environmental stability and the simple preparation by electrochemical polymerisation. An interesting property of PPy and other conducting polymers is that they undergo a volume change as the redox state is changed [1–4]. The volume change is due to the changes in the conformation of the polymer backbone, volume occupied by charge balancing counter ions, and the amount of solvent molecules present in the polymer matrix (osmotic expansion [5]). The redox state can be changed reversibly by electrochemical means, and consequently PPy can be used as a soft actuator driven by a small potential difference (1–2 V) [6,7].

An important property for materials to be used as actuators is the reversible strain. Previously, up to 2 or 3% strain in the length direction of a PPy film has been reported [4,8]. By the selection of an optimal doping ion (octyl benzene sulfonate) we have been able to increase the linear strain to 4% [9]. A much larger change in the direction of the thickness of the film has been reported [10,11], but this effect is difficult to utilise in an actuator.

It is well known that the synthesis conditions, such as the doping ion, electrolyte, and electrode materials, influences the properties of PPy. It is also known that for synthesis in aqueous solutions the micellar structure of the polymerisation electrolyte influences the properties of PPy films: Ouyang and Li [12,13] discovered that addition of a non-ionic surfactant to the electrolyte results in smoother, more flexible and stronger PPy films. Electrochemical properties were, however, not reported in this work. Experiment on PPy–DBS polymerisation just above and below the critical micelle concentration shows that the formation of micelles is important to the structure of the films. In the present work, we examine the effect of adding pentanol as a co-surfactant during polymerisation of PPy–DBS. The properties measured are conductivity, linear elongation, doping level together with the mechanical properties of the films. The effect of addition of pentanol to a sodium dodecyl sulphate (SDS) solution has been examined [14,15]. This system is expected to behave in a comparable way to a DBS solution. In both papers it was found that adding 0.5–1.7 vol%

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pentanol increases the micelle size, and produces large rod or wormlike micelles.

2. Experimental

Sodium dodecyl benzene sulfonate (NaDBS) (Aldrich, technical quality) and 1-pentanol were used as received. Pyrrole (Aldrich) was distilled under nitrogen and stored in the cold and dark prior to use. Aqueous solutions of 0.05 M NaDBS, 0.05 or 0.1 M pyrrole and between 0.0 and 7.4 vol% pentanol were used for polymerisation. The solutions with high pentanol concentration were cloudy due to large micelles, but apparently with only one liquid phase, although the 1-pentanol concentration was above the solubility in water (27 g dm^{-3}).

Free-standing PPy–DBS films were synthesised galvanostatically (1 mA cm^{-2}) on a polished stainless steel electrode, until a charge of 1.6 C cm^{-2} was deposited. This corresponds to a film thickness of approximately 10 μm. After synthesis, the films were rinsed with water, carefully removed from the steel electrode and dried at room temperature overnight. Conductivity was measured using the four-probe van der Pauw method [16]. Samples with a cloverleaf sharp were used to reduce the measurement error. Based on the calculated size of the error for the van der Pauw method given in Ref. [17], the error due to the van der Pauw method is estimated to be less than 1%.

The topography of the surface of the polymer films was examined with a Zeiss LSM 5 Pascal laser scanning microscope. Pictures are taken with a height difference of 0.4 or 1 μm, $x \times y$ resolution of 0.36×0.36 μm^2.

Mechanical properties were measured in a computerised force–displacement set-up consisting of a micrometer translation stage (Physik Instrumente), a microbalance, and an electrochemical cell fixed to the moving part of the translation stage. A feedback routine allows the application of a constant force to the film examined. The contribution of the spring constant of the set-up is accounted for in the Young's modulus, but it is of minor importance for the results as the error induced when neglected is less than 5%. Measurement of mechanical properties usually gives a large scattering, due to the differences in samples size and mounting. The electrolyte (0.2 M NaCl in water) was bubbled with nitrogen for ~15 min to reduce the amount of dissolved oxygen. The potential was measured against a saturated calomel reference electrode (SCE).

The change of mass of the PPy–DBS films during polymerisation and cycling was measured with an electrochemical quartz crystal microbalance (EQCM) using an ICM 10 MHz crystal with 0.2 cm^2 gold electrodes and controlled by a Hewlett Packard E4916A crystal analyser in combination with a potentiostat (Autolab PGSTAT 30). The quartz crystals were calibrated with Ag after the experiments, finding a proportionality constant of 0.96 ng Hz^{-1}, close to the 0.904 ng Hz^{-1} predicted by the Sauerbrey equation [18]. A Pt sheet was used as counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. For the EQCM experiments a film thickness of approximately 0.2 μm (6.4 mC total) was used.

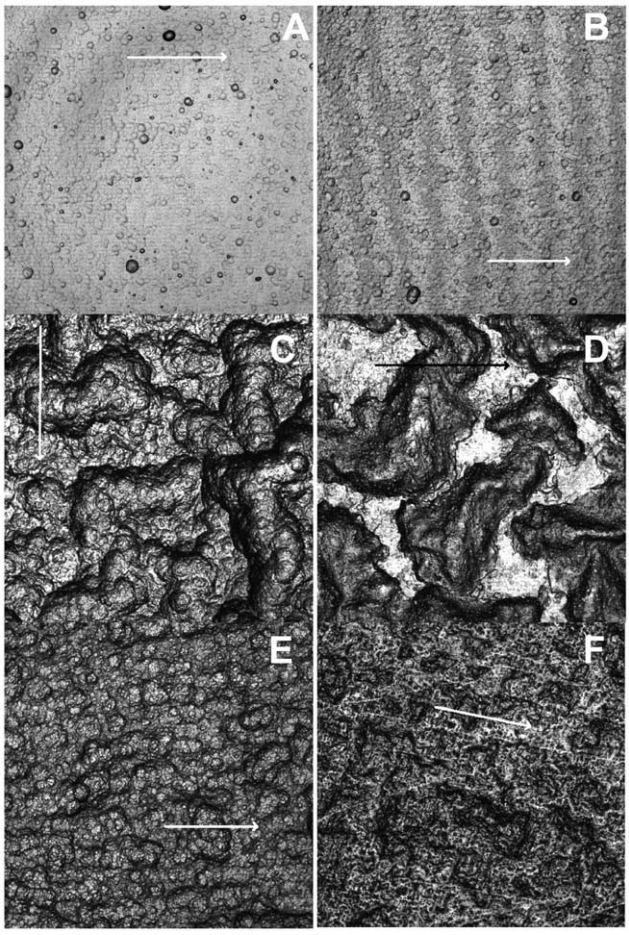

Fig. 1. Morphology of dry as-synthesised 10 μm thick PPy–DBS films. The sizes of all pictures are 185×185 μm^2: (A) no pentanol, (B) 0.8% pentanol, (C) 2.4% pentanol, (D) 2.4% pentanol side of film towards the steel electrode during polymerisation, (E) 4.0% pentanol, (F) 4.0% pentanol side of film towards the steel electrode during polymerisation.

3. Results and discussion

Figs. 1 and 2 show the morphology of 10 μm thick PPy–DBS films. The area covered by the pictures are 185×185 μm^2. The periodic stripe pattern on the pictures of PPy–DBS with 0.0 and 0.8% pentanol is an artefact from the electronic reconstruction from a series of pictures taken at different depths.

Films polymerised with no and with only 0.8% pentanol appear shiny and smooth to the eye, but have a few 'nodules' on the surface of a compact polymer layer. The nodules are a little larger and more distinct for the film prepared from a solution with 0.8% 1-pentanol than for the film prepared without pentanol. The variations in height

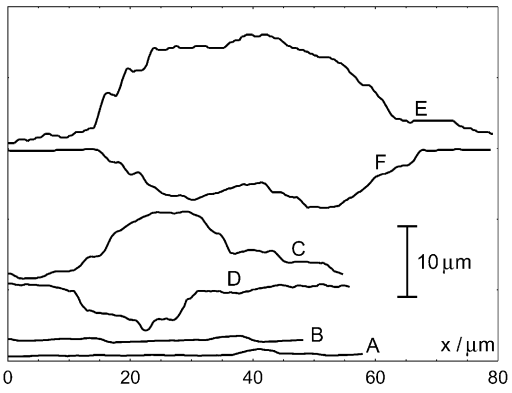

Fig. 2. Surface profile along the lines in Fig. 1. Scale on *x*-axis is along the lines. Scale on *y*-axis is indicated on the bar.

are around 1 and 0.5 μm, respectively. Both these films are flat on the backside—the side in contact with the stainless steel electrode during polymerisation.

The films prepared from solutions with 2.4 and 4.0% pentanol both appear dull or lustreless. On the picture it is seen that the nodules now totally dominate the surface, and the profile along the drawn line shows height differences that are of same magnitude as the nominal thickness of the film, 10 μm. The backside of the film is not flat, but shows large voids where the film has become detached from the electrode surface during the synthesis. This means that the film is buckling up and down, and it seem that for the synthesis with 2.4% pentanol added, only around half of the film kept contact to the electrode surface throughout the polymerisation. The profile of the film prepared with 4.0% pentanol, added to the synthesis solution also shows large height variations. The scale of the nodule structure is smaller than the 2.4% film, and it is difficult to see how much of the film have kept contact with the electrode during synthesis.

The results on the conductivity and mechanical test of PPy–DBS films prepared from solutions with 0.05 and 0.1 M pyrrole are shown in Tables 1 and 2. The conductivity and the Young's modulus of the dry films are measured on the as-synthesised oxidised film after they have been dried for 1 day at room temperature. The remaining measurements are made in electrolyte (0.2 M NaCl) after several reduction/oxidation cycles. The properties of PPy–DBS in the reduced state was measured at −0.9 V versus SCE and the oxidised state at 0.2 V versus SCE.

The conductivity of PPy–DBS prepared from a 0.05 M pyrrole solution will decrease for small concentration of pentanol added, but increase to the original value for higher concentrations. A synthesis solution with 0.1 M pyrrole gives a higher conductivity, which remains unaffected of the pentanol concentration. The tensile strength and the strain at failure are also higher for PPy–DBS prepared from the 0.1 M pyrrole solution. The simultaneous increase of conductivity and strain at failure indicates that PPy–DBS prepared from this solution contains fewer defects compared to the polymer made in the more dilute solution. A further increase of the pyrrole concentration in the synthesis electrolyte does not seem to affect the properties of PPy–DBS.

The Young's moduli are somewhat scattered, therefore a clear effect of the pyrrole concentration cannot be established. The Young's moduli of the wet films seem to be slightly lower for the larger pentanol concentrations—the

Table 1
Properties of PPy–DBS film polymerised from 0.05 M NaDBS, 0.05 M pyrrole and the given pentanol concentrations

Pentanol (vol%)	Conductivity (S cm^{-1})	Young's modulus (GPa)			Tensile strength (MPa)	Strain at failure (%)
		Dry	Oxidised	Reduced		
0.0	12.8	1.82	0.54	0.18	17	12
0.4	9.1	0.97	0.60	0.23	19	16
1.6	9.7	1.07	0.56	0.21	24	31
2.4	10.4	0.56	0.34	0.14	14	20
3.2	11.5	0.81	0.33	0.13	11	12
4.0	12.8	0.60	0.40	0.15	16	16

Table 2
Properties of PPy–DBS film polymerised from 0.05 M NaDBS, 0.1 M pyrrole and the given pentanol concentration

Pentanol (vol%)	Conductivity (S cm^{-1})	Young's modulus (GPa)			Tensile strength (MPa)	Strain at failure (%)
		Dry	Oxidised	Reduced		
0.0	19.8	1.11	0.40	0.18	22	46
0.8	23.1	1.75	0.59	0.19	28	45
1.6	21.4	1.25	0.51	0.17	23	35
2.4	23.8	0.72	0.50	0.17	26	41
4.0	23.0	0.60	0.39	0.16	21	44

effect being most apparent in the reduced state. For the dry films there is a drop in Young's modulus for pentanol concentration of 2.4% or higher. Since these are the same concentrations that yield the buckling films, it is reasonable to ascribe the lower Young's moduli to the morphology of the film and not to the changes in the polymer matrix. This is supported by the fact that the same large difference in stiffness is not seen for the wet films, and that the irreversible change in length that are seen in the first redox cycle increase from 0.5% for no pentanol to 1.2% for 4% pentanol added to the synthesis electrolyte. All these observations indicate that with a high concentration of pentanol in the synthesis solution, the adherence to the electrode decreases, and the PPy–DBS film are produced in a buckled shape, which is flattened during the first redox cycle under load.

During the electrochemical synthesis, polypyrrole is partially oxidised, and charge compensating ('doping') dodecyl benzene sulphonate ions are incorporated in the resulting polymer film. The doping level, α, of PPy–DBS is calculated from the frequency change of the oscillating quartz crystal (EQCM) during polymerisation, $\mathrm{d}f/\mathrm{d}t$. If we assume only pyrrole and DBS^- ions are incorporated in the polymer film:

$$\alpha = \frac{MW_{Py} - \frac{2F}{i}\frac{df}{dt}\beta}{\frac{F}{i}\frac{df}{dt}\beta - MW_{DBS}} \quad (1)$$

where $MW_{Py} = 67.09\ g\ mol^{-1}$ and $MW_{DBS} = 325.49\ g\ mol^{-1}$ are the molar masses of pyrrole and DBS^-, respectively, F the Faradays constant; i the polymerisation current, and β the proportionality constant between frequency and mass. It is assumed here that water and pentanol are not incorporated into the film during polymerisation. This assumption can be questioned, but the PPy–DBS seems to be hydrophobic until first reduction, where it takes up both ions and water. If water is present in the film, its effect will show up as an increase of the effective molar mass of the doping ions (DBS^-) and consequently, if this is not taken into account, the calculated doping level will be too high.

The doping level can also be found from the charge involved in the redox cycling of PPy–DBS:

$$\alpha = \frac{2\,q_{red}}{q_{poly} - q_{red}} \quad (2)$$

where q_{red} is the charge used in the first reduction of PPy–DBS, and q_{poly} is the charge used in the polymerisation. In this case incorporation of water molecules into the polymer film does not influence the result. The doping levels calculated from both the mass change and from the charge are plotted against the amount of pentanol in Fig. 3. Both the values based on the EQCM experiments and the values based on charge measured on a free-standing film show a maximum close to 2–3 vol% pentanol. The values are lower for free-standing films than for the films deposited on the quartz crystal's gold electrode. The reason is that the free-standing films are not fully reduced, because of a combination of low conductivity of the reduced PPy and a competing re-oxidation by oxygen dissolved in the electrolyte [19]. The highest values are those calculated from the mass change during polymerisation. This can be due to a true difference between the amount of dopant ions introduced during synthesis and the amount that can be cycled afterwards, e.g. if neutral NaDBS is incorporated in the polymer during synthesis, this will add to the mass, but not to the redox capacity. Alternatively, the reason can be that water and/or pentanol is incorporated together with DBS^- during the synthesis. The measured difference corresponds to an extra molar mass in addition to the DBS^- ions of $60–150\ g\ mol^{-1}$, with the highest values around 2.4% pentanol. Hence, it is not clear from these data whether pentanol works solely as a co-surfactant influencing the structure of the polymerisation electrolyte, or whether it is incorporated to some degree into the polymer. It might be expected that pentanol is removed from the polymer when it is rinsed with water or in case of the free-standing films when they are dried.

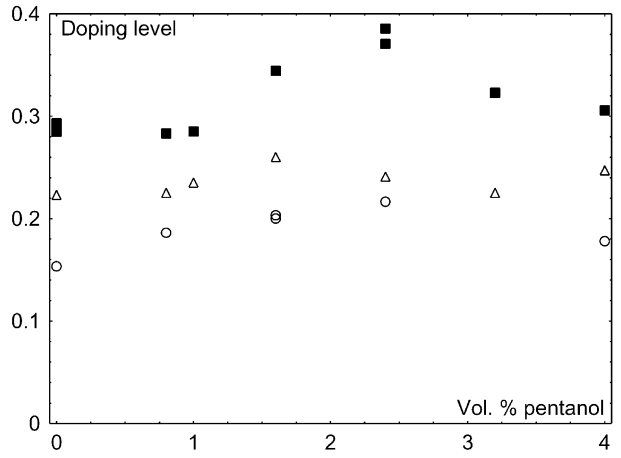

Fig. 3. Doping level for different PPy–DBS preparation. (○) free-standing 10 μm thick films, doping level calculated from cycling charge at 2 mV s^{-1}; (■) 0.2 μm films on Au electrode (EQCM), doping level calculated from mass change during synthesis; (△) 0.2 μm films on Au electrode (EQCM), doping level calculated from cycling charge at 10 mV s^{-1}.

The reversible linear length change between the reduced and oxidised states of the polymer is measured at a constant load of 0.6 MPa. The results are shown in Fig. 4. For the polymers prepared without pentanol addition, the strain is around 2.5% regardless of the pyrrole concentration in the synthesis electrolyte. For 0.1 M pyrrole in the synthesis electrolyte, the elongation of the polymer films increases with increasing amount of pentanol until 2.4 vol%, where a constant level of 5.6% strain is reached. For 0.05 M pyrrole a constant level of 4.5% is reached at about the same pentanol concentration. A single experiment not reported here, shows that, even higher concentration of pyrrole did not give a further improvement in strain. A few additional

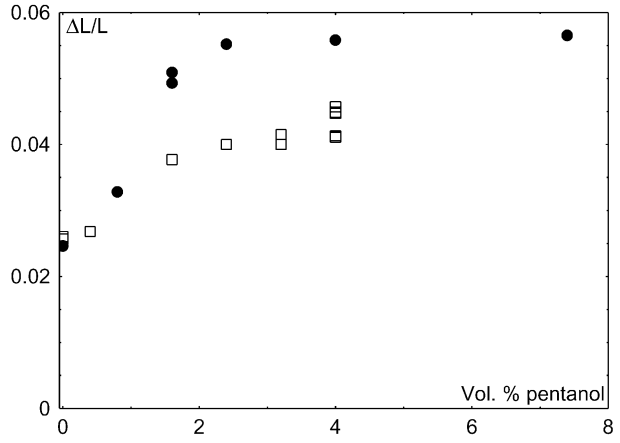

Fig. 4. Reversible linear strain for free-standing PPy–DBS films in 0.2 M NaCl polymerised at different synthesis concentrations. The concentration of NaDBS: 0.05 M; concentration of pyrrole: (□) 0.05 M, (●) 0.1 M; vol% pentanol given on the *x*-axis.

experiments not reported here also indicate that hexanol addition has a similar effect as pentanol.

Considering the lower stiffness and the higher doping level of PPy–DBS films prepared in a pentanol containing electrolyte the increased strain is not unexpected. On the basis of the model proposed in Ref. [5], the films prepared with the higher pentanol concentrations would be expected to show approximately 1% more strain, but an actual increase of 3% is observed! One reason for this improved performance could be that a larger change of the PPy conformation (intrinsic expansion) is induced by the changes in synthesis conditions. Alternatively the reason could be that the large buckling of the film has the effect that a part of the large change in thickness will be transformed into a change in the length of the film. In the EQCM experiments on 0.2 μm thick (0.2 cm^2) PPy–DBS films, the mass change in the first reduction was close to 1.9 μg regardless of the amount of pentanol added to the synthesis electrolyte, compared to a mass of 5 μg of the as-synthesised film. After a few redox cycles, the mass change during cycling begins to depend on the pentanol concentration at synthesis. Fig. 5 shows the mass change during the 11th cycle decreasing as the pentanol concentration is increased. This is in contrast to the results from the expansion measurements mentioned earlier, where a higher pentanol concentration results in a film showing a larger strain. This discrepancy can only be explained if a change in the anisotropy of the PPy–DBS films is assumed. As mentioned earlier, a very large expansion (up to 30%) has been observed in the direction perpendicular to the substrate for thin PPy–DBS films deposited on gold [10,11]. A large part of the total volume expansion thus does not contribute to the length change—probably because of a very anisotropic modulus. It is reasonable to assume that this anisotropy will not be maintained to the same degree in the buckled film prepared in the presence of pentanol. With a more isotropic expansion it is then feasible to obtain an increased length change although the overall volume change is smaller.

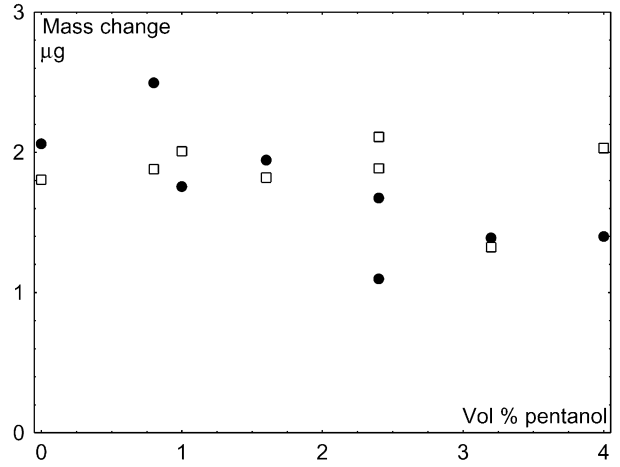

Fig. 5. Mass change from oxidised to reduced state for PPy–DBS on Au (0.2 μm thick, 0.2 cm^2): (□) during the first reduction; (●) in cycle no. 11.

4. Conclusion

In this work, the addition of 1-pentanol as a co-surfactant to the aqueous polymerisation electrolyte used for preparation of PPy–DBS is investigated. The alcohol is only incorporated in the polymer to a minor degree, but nevertheless has a marked influence on the morphology and actuator properties of the polymer. The use of more than 2.4 vol% 1-pentanol increases the reversible linear strain from 2.5 to 5.6%. The reason for the higher strain is partly a higher doping level combined with a small decrease in stiffness, but apparently a more advantageous morphology of the PPy–DBS film is the major factor. The strength and conductivity of the polymer film is almost unchanged by the pentanol addition. The large increase in strain outweighs the small decrease in stiffness, and PPy–DBS prepared with pentanol as co-surfactant in the polymerisation electrolyte showed a considerably better performance than the material prepared without pentanol.

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