Macromolecules **2002,** *35,* 9345−9351

Polypyrrole Doped with Alkyl Benzenesulfonates

Lasse Bay,*,†,‡ Naja Mogensen,† Steen Skaarup,† Peter Sommer-Larsen,‡
Mikkel Jørgensen,‡ and Keld West‡

Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark, and
The Danish Polymer Centre, Risø National Laboratory, DK-4000 Roskilde, Denmark

Received May 13, 2002; Revised Manuscript Received September 23, 2002

ABSTRACT: The properties of polypyrrole (PPy) are to a large extent determined by the condition of synthesis and especially by the counterion incorporated as dopant during synthesis. In this work, PPy doped with different alkyl benzenesulfonates are compared. The polymer films are prepared by constant current oxidation of pyrrole in aqueous solutions containing sodium benzenesulfonates having alkyl chain lengths between 1 and 22 carbon atoms. The doping levels of the polymers are evaluated both electrochemically and by means of a quartz crystal microbalance. The mechanical properties of free-standing films of the materials (tensile strength and Young's modulus) together with the reversible linear elongation between the oxidized and reduced states are determined. A maximum in linear elongation of 4% is found for *p*-(*n*-octyl)benzenesulfonate, and the highest electronic conductivity is found for *p*-(*n*-butyl)benzenesulfonate.

Introduction

Conducting polymers—for instance polypyrrole (PPy)—can be reduced and oxidized reversibly by changing the electrochemical potential by less than 1 V. Under this redox change, the polymer will take up ions for charge compensation, and solvent molecules may be driven in from the surrounding electrolyte due to osmotic forces. This causes a volume change of the polymer, which can be utilized in soft polymer actuators or "artificial muscles" controllable in a narrow voltage range.[1−3] These materials, however, still need to be improved with respect to the maximum linear elongation (which is presently only a few percent) and to be optimized with respect to mechanical properties such as stiffness and creep stability to realize polymer actuators with a viable performance.

Electrochemically polymerized PPy is formed in the oxidized state and will contain charge-compensating anions incorporated during synthesis. Many different anions can be used as dopants, e.g., ClO_4^-, Cl^-, NO_3^-, toluenesulfonate (TS^-), and dodecyl benzenesulfonate (DBS^-).[4−9] The properties of PPy are strongly influenced by the nature of the doping anions. When doped with large anionic detergents, PPy shows a much higher chemical stability in aqueous systems compared with PPy doped with smaller anions. Previously, two alkyl benzenesulfonates, DBS^- and TS^-, have been tested in aqueous media[4] and a few more in nonaqueous media.[6] A systematic investigation of the influence of the size of the dopant anion has been made for PPy doped with alkyl sulfates and sulfonates having chain lengths from C_4 to C_{18}.[10,11]

Because of the large difference in the lengths of the alkyl chains, salts of TS^- and DBS^- have very different solubility properties. While NaTS dissolves as a conventional salt in water, DBS^- is amphiphilic, and NaDBS will aggregate in aqueous solutions to form micelles above the critical micelle concentration (cmc). Commercial grades of NaDBS are mixtures of isomers and homologues with cmc close to 1 mmol dm^{-3}.[12,13]

Using either TS^- or DBS^- as dopants, PPy films can be polymerized electrochemically from aqueous electrolytes with a current yield of almost 100% in a dense quality suited for making free-standing films. With DBS^- particularly smooth and chemically stable polymer films are obtained, whereas TS^- gives polymers with a higher conductivity but lower stability. The smaller TS^- ion is mobile in the polymer, and when the polymer is cycled between the oxidized and reduced states, TS^- anions will to some extent participate in the charge compensation reactions and migrate out of the polymer. As both anions and cations move in PPy doped with TS^-, the total ion flux due to charge compensation will be made up of opposing cation and anion fluxes. This will lower the total volume change of the polymer as the volume change is connected to the change in total ion concentration in the polymer.[14] The larger DBS^- ions, on the other hand, are virtually immobile and will stay in the polymer over hundreds of reduction/oxidation cycles. Therefore, cations from the surrounding electrolyte will dominate the charge compensation, moving in to and out of the polymer when it is redox cycled. In this way the mechanical response is maximized.

In the present paper, alkyl benzenesulfonates with chain lengths of the alkyl group between C_1 and C_{22} are investigated as doping ions in PPy with regard to doping degree (the ratio between dopant ion and polymer repeating unit), conductivity, mechanical properties, and linear elongation. Up to C_8 the *n*-alkyl benzenesulfonates are used. For the larger alkyl groups, the solubility at room temperature of *n*-alkyl benzenesulfonates is low as the Krafft temperature is above room temperature. Thus, for C_{12} and above, isomers with benzene linked to a secondary carbon atom in the alkyl chain are used, as this increases the solubility of the detergents without changing the volume of the anion.

Experimental Section

Sodium *p*-toluenesulfonate (NaTS) from Merck and sodium 4-(oct-1-yl)benzenesulfonate (NaOBS) from Aldrich are used

---

† Technical University of Denmark.
‡ Risø National Laboratory.
* Corresponding author: e-mail lasse.bay@risoe.dk.

10.1021/ma0207327 CCC: \$22.00

as received. The sodium salts of 4-(but-1-yl)benzenesulfonic acid (NaBBS),[15] 4-(hex-1-yl)benzenesulfonic acid (NaHBS),[16] 4-(dodec-2-yl)benzenesulfonic acid (Na(2D)BS),[17] 4-(dodec-6-yl)benzenesulfonic acid (Na(6D)BS),[18] and 4-(hexadec-8-yl)-benzenesulfonic acid (NaHDBS)[19] were prepared according to literature procedures. The sodium salt of 4-(docos-11-yl)-benzenesulfonic acid (NaDCBS) was prepared using a procedure similar to that used for 4-(hexadec-8-yl)benzenesulfonic acid. The products were recrystallized from ethanol–water mixtures, and the content of small inorganic ions was checked by ion chromatography to be below 10 ppm. Pyrrole from Aldrich was distilled under nitrogen and stored in the dark and cold prior to use.

PPy films are prepared by electrochemical polymerization from aqueous solutions of 0.05 M pyrrole and 0.05 M sodium alkyl benzenesulfonate. The solutions with NaHDBS and NaDCBS are viscous and turbid, consistent with concentrated aqueous solutions of these detergents being in equilibrium with surfactant-rich, hydrated liquid-crystalline phases.[20] Free-standing films of PPy are formed on the surface of a polished stainless steel electrode using an oxidation current density of 1 mA cm^{-2}. For NaDCBS, however, polymerization is only possible at a current density of 0.5 mA cm^{-2} or lower. The reason is that a thick gel is formed around the electrode lowering the diffusion rate of reactants to the electrode. NaHDBS was prepared at both current densities. The as-prepared oxidized films are peeled off the steel electrode and dried in the ambient for 1 day prior to the measurements. The thickness of the PPy films is controlled by the charge passed during polymerization. For all free-standing films the charge is 1.6 C cm^{-2}, which for PPy–DBS films corresponds to a film thickness of 10 μm as measured by a Dektak profilometer.

The in-plane conductivity of the dry films is measured by the four-probe van der Pauw method[21] at room temperature. Cloverleaf-shaped samples were used to reduce the errors of measurements to less than 1%.[22]

A force–displacement setup is used to measure the mechanical properties and the length change when PPy is oxidized and reduced electrochemically. In this setup, a strip of the free-standing film under examination is attached mechanically at both ends and electrically at one end. Typical dimensions of the exposed part of the strips are 5 mm (length) × 3 mm (width). The Young's modulus or stiffness of the polymer films is determined from the slope of the recorded force vs displacement curves in the initial range where the curve is linear. The measured values are corrected for the contribution of the inherent spring constant of the setup. This correction is small, and the error induced if it is neglected is less than 5%.

In the setup, the films can be immersed in an electrolyte (0.1 M NaCl in water), which is continuously bubbled with nitrogen to lower the amount of dissolved oxygen. The potential is measured against a saturated calomel reference electrode (SCE), and the stretching of the film is controlled by the position of a translation stage (Physik Instrumente). Via a feedback routine from an electronic balance measuring the force acting on the polymer to the translation stage, a constant force can be applied to the film. The setup is described in more detail elsewhere.[23]

An electrochemical quartz crystal microbalance (EQCM) was used to measure changes in the mass of PPy films during polymerization and cycling. The EQCM consists of a 10 MHz crystal with 0.2 cm^2 gold electrodes (ICM) and controlled by a Hewlett-Packard E4916A crystal analyzer in combination with a potentiostat (Autolab, PGSTAT 30). The quartz crystals were calibrated by silver deposition, and the resulting proportionality constant, 0.96 ng Hz^{-1}, is close to the 0.904 ng Hz^{-1} predicted by the Sauerbrey equation.[24] In this setup a platinum sheet was used as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. For the EQCM experiments a polymer film thickness of approximately 0.2 μm (6.4 mC deposited during polymerization) was used, except for DCBS$^-$ where a charge of 3.2 mC was used.

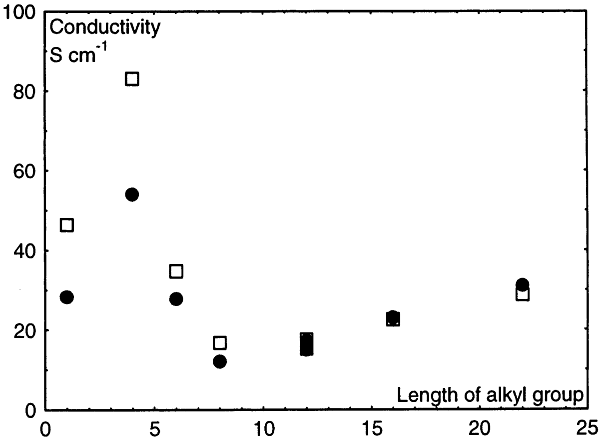

Figure 1. Conductivity of dry PPy film doped with different alkyl benzenesulfonate anions. The lengths of the anion alkyl group are specified on the *x*-axis. (●) Thickness based on a nominal thickness of 10 μm (160 mC cm^{-2} μm^{-1}). (□) Thickness calibrated with profilometer.

Results and Discussion

Conductivity. The electronic conductivities measured on dry films are shown in Figure 1 as a function of the size of the dopant anion. The conductivities are given both based on the geometric dimensions of the films and based on a nominal thickness of 10 μm. This is the experimental thickness measured on PPy–DBS films deposited with 1.6 C cm^{-2}. The proportionalities between thickness and polymerization charge measured for the other doping anions are the following: TS$^-$, 0.26 C cm^{-2} μm^{-1}; BBS$^-$, 0.25 C cm^{-2} μm^{-1}; HBS$^-$, 0.20 C cm^{-2} μm^{-1}; OBS$^-$, 0.22 C cm^{-2} μm^{-1}; HDBS$^-$, 0.16 C cm^{-2} μm^{-1}. For the smaller doping anions these values are close to the 0.24 C cm^{-2} μm^{-1} usually cited for small doping anions.[25,26] Measurement of foil thickness is, however, much less accurate than measurement of charge, and as we want to compare the properties of the PPy backbone, we have chosen in the following to use a nominal thickness based on 0.16 C cm^{-2} μm^{-1} for all polymers. The amount of PPy polymer per unit area and nominal volume are thus the same for all the films compared here, apart from a minor deviation caused by variations in the doping degree after synthesis.

The highest conductivity, 83 S cm^{-1}, was found for PPy–BBS. The decrease in conductivity from BBS$^-$ to OBS$^-$ can be explained by the fact that larger dopant anions will result in larger distances between the PPy strands and hence a higher resistance to interchain jumping. The low conductivity of PPy–TS may be linked to the considerably lower chemical stability of this polymer in aqueous systems compared to for example PPy–DBS. Although we still need better structural evidence, our belief is that the amphiphilic nature of the longer alkyl benzenesulfonates leads to a structuring of the polymer–detergent complexes, which causes the aging reactions that occur in the presence of water and oxygen to be significantly suppressed.

The conductivity of PPy prepared with long chain length alkyl benzenesulfonates (from OBS$^-$ to DCBS$^-$) increases with the length of the alkyl chain. As the interchain conductivity is expected to decrease with the size of the dopant, this effect must be more than compensated by an increase in the intrachain contribution to the conductivity. Again, this effect is contributed to the propensity of the dopants to structure their environment. The higher structuring tendency of the

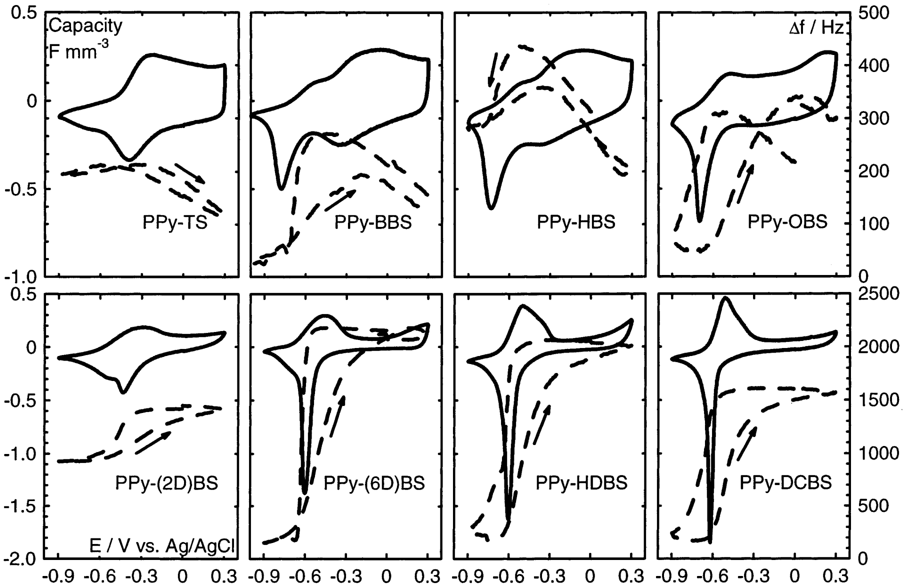

Figure 2. Voltammograms (solid line) and mass change (dash line) of 0.2 μm films doped with the anions indicated in the figure in 0.1 M NaCl. The sweep rate is 10 mV s^{-1}. The ordinate to the left is the capacity in F mm^{-3}. The ordinate to the right is the mass change given as frequency change (the proportionality constant is 0.96 ng Hz^{-1}). Note the scales on upper and lower row graphs are different. The abscissa is the potential in V vs SCE. The scales on the abscissa are the same on all the graphs.

longer chain alkyl sulfonates is expected to lead to a more structured polymer, where a larger part of the current can be transported in ordered domains.

Wernet et al.[10,11] have measured the conductivity of PPy doped with alkyl sulfonates and sulfates with different chain lengths (C_4 to C_{16}) and find a maximum in conductivity for the chain length 8. Allowing for the size of the benzene group, the finding in the present work of a maximum at a shorter chain length is not surprising. Warren et al.[4] used almost the same synthesis conditions as here and report conductivities for both PPy−TS and PPy−DBS that mainly differ from those given in Figure 1 due to a different assignment of the thickness of the polymer. Much higher values of the conductivity of PPy−TS are obtained for nonaqueous synthesis, e.g., 300 S cm^{-1} for polymerization in acetonitrile.[27]

Voltammograms. Figure 2 shows cyclic voltammograms and EQCM responses for 0.2 μm films on gold cycled in 0.1 M NaCl electrolyte. To facilitate comparison of cyclic voltammograms on redox electrodes, current can be normalized with the sweep rate. In the resulting differential capacity vs voltage diagrams, the area under the curves is a direct measure of the charge that is cycled in and out of the polymer. In cases where polymer electrodes of different sizes are compared, the current can be further normalized with the volume of the polymer to give the specific differential capacity (units: F mm^{-3}).

The first oxidation peak (at the lowest potential) is linked to movement of cations out of the polymer, which can be seen from the increase in EQCM frequency corresponding to a decreasing electrode mass. Some of the voltammograms have a second broad oxidation peak. This second oxidation peak has been ascribed to anion movement[28] taking over when the number of charges on the polymer exceeds the number of bound anions left in the polymer. This assumption is confirmed by the EQCM traces, showing an increasing electrode mass in these ranges. With the larger dopant ion, cation movement becomes dominating compared to anion movement, because the larger dopant anions are more strongly bound to the polymer and thus are less prone to be replaced by smaller, mobile chloride anions. With the largest dopant ions, only cations move in and out of the polymer during cycling.

Although the oxidation reaction is spread out over several hundred millivolts, the reduction reaction occurs in a narrow potential range. This is not a kinetic effect, as the capacity curves do not change much with decreasing sweep rate. We ascribe this hysteretic behavior to changes in conformation. On oxidation the charged polymer and the corresponding counteranions relax into a tight coordination, in which the polymer−anion complex is stabilized. Recreation of the open, water-swelled structure of the polymer in the reduced state is a cooperative process involving the simultaneous participation of several polymer segments. Because of the stabilization, the reduction potential is shifted to more negative potentials, and the cooperative nature causes the reaction to occur in a narrow potential range. Some of the voltammograms on materials with simultaneous cation and anion mobility show an additional, smaller reduction peak because of the more complex reaction scheme for these materials. The reduction potentials for free-standing films are as follows (scan rate of 2 mV s^{-1}): −0.4 V for HBS$^-$, OBS$^-$, and (2D)BS$^-$; −0.5 V for (6D)BS$^-$; −0.6 V for BBS$^-$ and TS$^-$; −0.7 V for HDBS$^-$; and −0.8 V for DCBS$^-$ all vs SCE.

Degree of Doping. The ratio between dopant ion included in the polymer as counterions and the polymer monomer—the degree of doping—can be estimated from the weight changes during polymerization if one assumes that water and neutral salt are not incorporated into the polymer to a significant extent during synthesis. As two electrons are required for the incorporation of one monomer unit and one electron for each dopant molecule, the ratio between dopants and monomers can then be calculated from the weight change and charge consumption during synthesis. The results are shown in Figure 3. Alternatively, the degree of doping can be found from the capacity of the PPy films, which is the amount of charge that can be cycled in and out of the polymer in the voltage range considered. For the EQCM

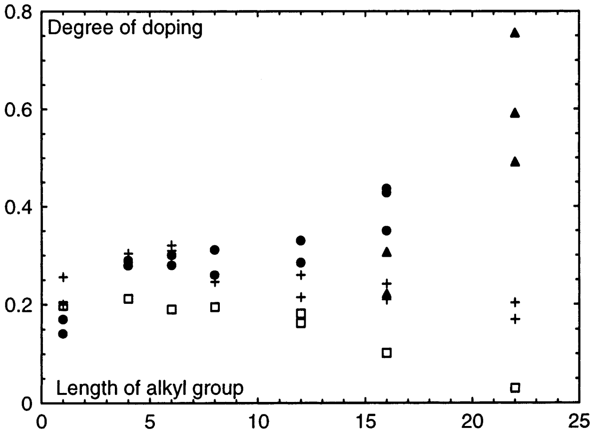

Figure 3. Degree of doping of PPy for the different doping ions. (●) Calculated from mass change during polymerization at 1 mA cm^{-2}. (▲) The same but for 0.5 mA cm^{-2}. (+) From the reduction charge of films deposited on EQCM electrodes. (□) From the redox charge of free-standing films.

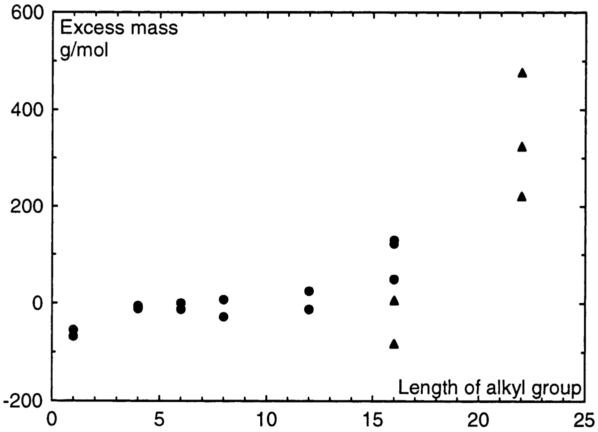

Figure 4. Excess mass of neutral molecules following the doping anions during polymerization, calculated from the EQCM measurements assuming a constant doping degree of 0.3. (●) For synthesis current 1 mA cm^{-2}. (▲) For synthesis current 0.5 mA cm^{-2}.

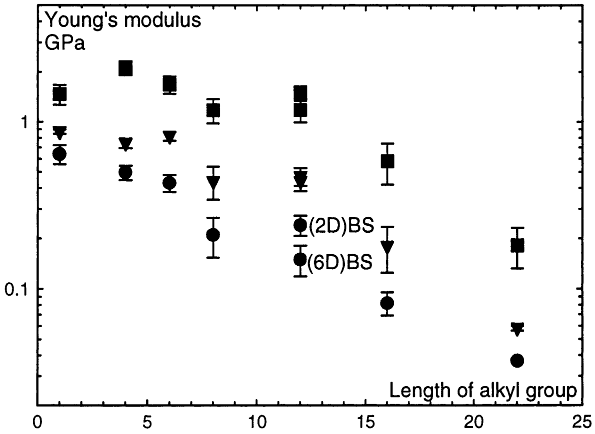

Figure 5. Young's moduli (stiffness) of PPy films. The number of carbon atoms in the alkyl group of doping anion is on the *x*-axis. (■) Dry oxidized films. (▼) Oxidized films (0.0 V vs SCE) in 0.1 M NaCl. (●) Reduced films (−0.9 V vs SCE) in 0.1 M NaCl. Error bars from 3 to 5 samples.

electrodes where the polymer film is in good electronic contact with the gold substrate, it is most accurate to base the calculations on the charge consumed in the first reduction, as the capacity decreases somewhat in the following cycles due to partial inactivation and because of the possibility of oxidation beyond the point where the charge on the polymer balances the amount of alkyl benzenesulfonate ions incorporated into the polymer. The free-standing films, however, cannot be completely reduced due to low conductivity of the film in the reduced state.[29] The capacity increases, however, during the first cycles because the charge percolation along the length of the polymer strip becomes more efficient. For these films the maximum capacity is used, although it still underestimates the degree of doping. As can be seen in Figure 3, the values determined in this way are lower than the values determined by the other methods.

For free-standing films the estimated doping degree is almost constant for the smallest anions, approximately 0.2 e$^-$ per monomer, and decreases for the larger anions. Especially, the PPy−DCBS film has a very low capacity as only 0.03 e$^-$ per monomer can be cycled. As expected, more charge can be cycled in the polymer films deposited on EQCM electrodes. The variation with composition is relatively small, with a maximum of 0.3 for HBS$^-$ and decreasing toward 0.2 for both higher and lower chain lengths.

For the small anions the degrees of doping found from the mass changes during polymerization yield the same results as those found from the voltammograms. This indicates that all affected pyrrole units can be redox cycled reversibly and that only doping anions are incorporated in the polymer during synthesis. For the larger ions DBS$^-$, HDBS$^-$, and DCBS$^-$ a large apparent increase in the doping degree determined from mass changes is seen. This increase is probably an artifact because of an excess mass following the doping ions, e.g., water or more likely undissociated sodium alkyl benzenesulfonates. The tendency for incorporation of neutral molecules in the polymer is expected to increase when the hydrophobic fraction of the polymer increases. If we assume that the doping degree has a constant value of 0.3, this excess mass can be calculated (see Figure 4). The figure shows that the amount of tenside in PPy−DCBS is more than twice the amount used for charge compensation, whereas no additional mass seems to be incorporated in PPy doped with anions smaller than HDBS$^-$. When comparing the two syntheses of PPy−HDBS at different current densities, it is found that a higher excess mass is encapsulated in the polymer at the higher current density.

The rate of the weight changes during polymerization is constant for the dopants used, except for DCBS$^-$, where a change from 150 Hz s^{-1} initially to 110 Hz s^{-1} at the end of the synthesis is observed, and for HDBS$^-$ deposited with a current density of 1 mA cm^{-2}, where the changes is from 210 to 150 Hz s^{-1}. This shows that the composition of these polymer materials gradually varies during deposition with an increasing fraction of pyrrole as the layer becomes thicker. This is one reason for the large scatter in Figure 2 between the doping degrees of PPy−DCBS estimated by different methods.

Mechanical Properties. The Young's moduli measured for the dry oxidized films are shown in Figure 5. After the Young's modulus of the dry film is measured, the film is immersed in 0.1 M NaCl. The film then slowly becomes softer because of the plasticizing effect of the water uptake.[30] After an equilibration period of around 1000 s, the film is redox cycled several times between 0.4 and −0.8 V vs Ag/AgCl before the Young's moduli of the reduced and oxidized film are measured

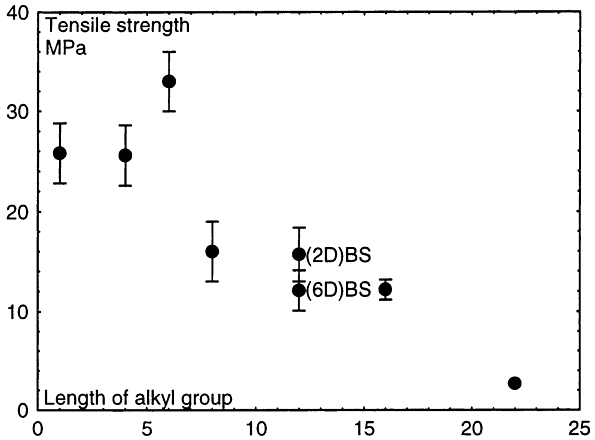

Figure 6. Tensile strength of PPy films in 0.1 M NaCl after cycling. The number of carbon atoms in the alkyl group of the doping anion is indicated on the *x*-axis. Error bars from 3 to 5 samples

in the wet state. Apart from the results for PPy−TS, the general trend seen from Figure 5 is that the stiffness decreases with increasing size of the doping anion. This can be attributed to an increased distance between the PPy backbones and to a larger proportion of the volume being filled by flexible alkyl groups rather than stiff polymer segments with conjugated double bonds. The negative deviation that PPy−TS shows from the general trend on Figure 5 is probably due to the lower stability in aqueous media shown by PPy doped with small anions without amphiphilic character. A previous study of PPy−TS[30] found values similar to those reported here for material prepared from an aqueous electrolyte (1.1 GPa for the dry material), whereas the material prepared in acetonitrile had a higher modulus (2.9 GPa in the dry state). The higher alkyl benzenesulfonates are only sparingly soluble in acetonitrile, and PPy films with these dopants cannot be synthesized from acetonitrile solutions.

Another general trend is that the decrease in stiffness on exposure to the aqueous electrolyte is larger for the larger doping ions: For the large dopants the Young's modulus of the wet, reduced film is only approximately 15% of that of the dry, oxidized state whereas this ratio increases to approximately 25% for the smallest anions, TS^-, BBS^-, and HBS^-. The Young's moduli of the wet, reduced films are approximately only half of that of the corresponding wet oxidized films. Variation of the elastic moduli of PPy with the redox state is reported earlier.[23,31,32] The two isomers $(2D)BS^-$ and $(6D)BS^-$ only give rise to a minor difference in the stiffness of the PPy films. This indicates that it is the total volume of the anion rather than its extension that is important for the properties of the PPy−ABS complex.

The ultimate tensile strength is measured on the polymer films in 0.1 M NaCl, after they are redox cycled several times (see Figure 6). For these tests a strain rate of 4×10^{-4} s^{-1} is used. With this low strain rate the measured tensile strengths are close to or identical with the breaking strength for the examined polymers. For the larger dopant ions the strength of the polymer decreases with increasing chain lengths of the alkyl group: from 30 MPa for PPy doped with the smaller anions to only 3 MPa for films doped with DCBS. The decrease in the tensile strength can be rationalized using the same arguments as given above for the decrease in the Young's moduli.

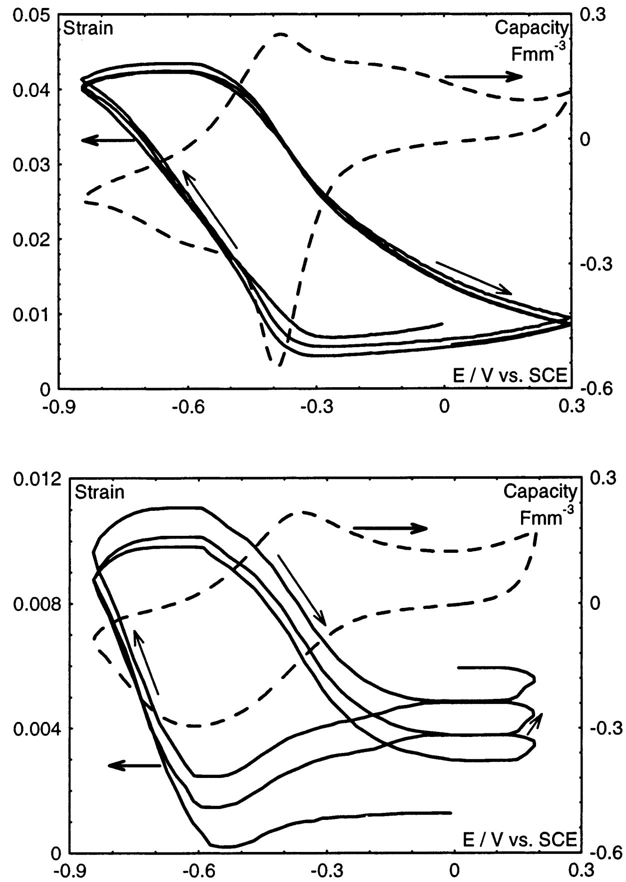

Figure 7. Strain and capacity vs potential of 10 μm free-standing PPy films in 0.1 M NaCl. The sweep rate is 2 mV s^{-1}. Polymer strip length is 5 mm. (A, top) PPy doped with OBS; (B, bottom) PPy doped with BBS.

Dimensional Change. The linear length change of PPy−OBS and PPy−BBS strips that are redox cycled in 0.1 M NaCl loaded with a constant force of 0.5 MPa is shown in Figure 7A,B together with the simultaneously obtained voltammograms. When PPy−OBS is reduced (reduction peak at −0.4 V vs SCE), the film elongates. This is mainly due to cations (and solvent) moving into the polymer from the surrounding electrolyte. During oxidization the cations will leave the polymer, leading to contraction of the polymer. The OBS^- anion is so large that it is practically immobile and stays in the polymer. The same behavior is found for the polymers doped with anions larger than OBS^-. The response of PPy−BBS (Figure 7B) is more complex. On reduction, PPy−BBS first contracts and then elongates. This behavior is consistent with the conclusions from the EQCM study that both anions and cations are mobile. In the initial stages of the reduction process, anions first leave the polymer and a contraction is observed. When the potential is further decreased, cations will start to enter the polymer, and polymer elongation is observed. As two different ions move, the reduction peak (at −0.6 V vs SCE) becomes wider. The behavior during oxidization is similar: At first the cations leave and the polymer contracts, and above 0 V vs SCE anions reenter the polymer. Mobility of the doping anions is also observed for the smaller anion TS^-. Previously mobility of TS^- in PPy−TS was observed by Pei et al.[33] using the bending beam method. Cycling of PPy−HBS initially shows the behavior typically of PPy with an immobile dopant similar to that seen in Figure 7A. On extended cycling in tenside free electrolyte,

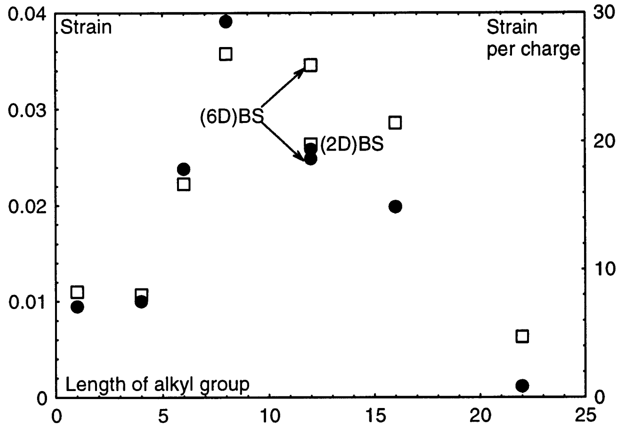

Figure 8. (●, left axis) Maximum contraction from the reduced (−0.85 V vs SCE) to the oxidized (0.2−0.3 V vs SCE) states of PPy films. (□, right axis) Contraction per charge density (units: mol of electrons $cm^{-3})^{-1}$ between the reduced and the oxidized states of the PPy films. The different doping anions are indicated on the *x*-axis by the lengths of their alkyl group.

however, the doping anions gradually leak out of the polymer, and the effect of anion movement can be seen on the linear elongation. When sweeping the potential between −0.85 and 0.3 V vs SCE, it takes 15−20 cycles for HBS$^-$ and only 1−4 cycles for BBS$^-$ before the mixed elongation scheme associated anion movement is observed with the force−displacement setup. For the larger doping anions no anion movement are observed even after hundreds of cycles.

In Figure 8 the overall strain obtained with PPy doped with different alkyl benzenesulfonate ions is shown; the strain is measured as the contraction of the film. There is a maximum in contraction (and elongation) of almost 4% for PPy−OBS. Doping of PPy with HBS$^-$ or smaller anions results in less elongation. Also shown in Figure 8 is the linear strain per charge density; the units are (mol of electrons $cm^3)^{-1}$. The corresponding volume change per mole of electrons can be estimated as 3 times the value for the length change if isotropic expansion of the polymer is assumed.

One cause of the maximum in strain is that the smaller dopant ions are (partly) mobile, resulting in opposing cation and anion motion and thus in a smaller total length change per charge. With the larger anions, a steady decrease in the strain is seen with increasing anion size. This is contrary to expectations, as the softening of the polymer with increasing dopant size should lead to an increase in the osmotic contribution to the expansion as long as all the charged particles inserted can be considered as independent entities. We have, however, already seen indications that with the largest anion, DCBS, a considerable amount of undissociated sodium alkyl benzenesulfonate is incorporated into the polymer during synthesis. The decrease in strain seen with the larger dopants is thus a reflection of an increasing tendency for ion−ion and ion−polymer association with increasing size of the anions. Assuming that osmotic expansion is the dominating effect responsible for the observed strain,[14] one can calculate that the effective number of independent particles in the PPy−HDBS system is only half the total number of cations and anions present, whereas it in the PPy−DCBS only is one out of four.

The data in Figure 8 are obtained using a constant sweep rate of 2 mV s^{-1}. Using lower sweep rates does not increase the strains further, showing that the maximum in strain seen here is not a kinetic effect, but rather an intrinsic materials property due to the specific mix of properties incurred by the dopant. PPy−OBS has the lowest dry state conductivity of the materials compared here and should hence be most prone to limitations by the competing oxygen reduction reaction.[29] However, the free-standing films of PPy−OBS are able to cycle a larger amount of charge per monomer than most of the other materials compared here. This is due to either a higher conductivity in the reduced state or the relatively high redox potential of PPy−OBS free-standing films. At the higher redox potential there is less competition from the oxygen reduction, so more of the film can be reduced and more charge per monomer can therefore be redox cycled.

PPy doped with the two different dodecyl benzenesulfonates, (2D)BS$^-$ and (6D)BS$^-$, gives nearly the same elongation. Hence, as for the mechanical properties, the total size of the alkyl chain seems more important than the length of the longest alkyl chain.

Conclusion

The properties of polypyrrole films doped with alkyl benzenesulfonates are examined, covering alkyl chain lengths between 1 and 22. The polymers are made by electrochemical oxidation, and during synthesis 0.25−0.3 mol of dopant per mole monomer is incorporated to balance the excess charge on the polymer backbone. The results indicate that, with the largest dopant anions studied here, an additional amount of undissociated sodium alkyl benzenesulfonate is built into the polymer during the synthesis. The small dopants show an appreciable mobility in the polymer matrix, and on electrochemical cycling of these polymers in a tenside free electrolyte, the dopant anions will gradually leak out and be replaced with chloride ions. The ionic mobility decreases, however, with the size of the anion, and the OBS$^-$ ion is the largest alkyl benzenesulfonate ion where mobility was detected in the EQCM experiments. The effect is however small, and with the thicker films used in the elongation tests, no signs of anion mobility was detected for hundreds of cycles.

The size of the doping anion influences many properties of the PPy−ABS complex. The electronic conductivity shows a complex behavior with maximum conductivity (83 S cm^{-1}) for PPy−BBS and minimum conductivity (16 S cm^{-1}) for PPy−OBS. As the size of the dopant anion increases, the distance between PPy chains increases. The lower interchain interaction leads to a decrease in both the tensile strength and the Young's modulus. It should be notice that the tensile strengths reported here is considerably lower than the numbers for polythiopene and polyaniline often used to estimate the potential of conducting polymers as actuators.[2]

Cycling of PPy doped with alkyl benzenesulfonates between the oxidized and the reduced states is accompanied by volume changes of the polymer. PPy−TS, which has a charge-compensating scheme dominated by anion movement, shows elongation on oxidation, whereas the PPy's doped with larger alkyl benzenesulfonates have dominating cation mobility and elongate on reduction. A maximum in reversible linear strain of 4% is found for PPy−OBS. The maximum in strain is not caused by a single material property as for example the conductivity or doping level, but the maximum can be seen as the result of a tradeoff between the desire to have immobilized anions and at the same time to keep the ion−polymer and ion−ion interaction as low as possible.

Acknowledgment. T. Mazur, O. Jørgensen, and H. D. Rasmussen of The Danish Polymer Centre are acknowledged for synthesis of the alkyl benzenesulfonates. The Danish Research Agency supported this work through the THOR program (Grant 9700882).

References and Notes

(1) Pei, Q.; Inganäs, O. *Adv. Mater.* **1992**, *4*, 277−278.
(2) Baughman, R. H. *Synth. Met.* **1995**, *78*, 339−353.
(3) Hutchison, A. S.; Lewis, T. W.; Moulton, S. E.; Spinks, G. M.; Wallace, G. G. *Synth. Met.* **2000**, *113*, 121−127.
(4) Warren, L. F.; Anderson, D. P. *J. Electrochem. Soc.* **1987**, *134*, 101−105.
(5) Takakubo, M. *Synth. Met.* **1987**, *18*, 53−55.
(6) Buckley, L. J.; Roylance, D. K.; Wnek, G. E. *J. Polym. Sci.* **1987**, *25*, 2179−2188.
(7) Vork, F. T. A.; Schuermans, B. C. A. M.; Barendrecht, E. *Electrochim. Acta* **1990**, *35*, 567−575.
(8) Yongfang, L.; Yongfa, F. *Synth. Met.* **1996**, *79*, 225−227.
(9) Yuan, Y. J.; Adeloju, S. B.; Wallace, G. G. *Eur. Polym. J.* **1999**, *35*, 1761−1772.
(10) Wernet, W.; Monkenbusch, M.; Wegner, G. *Macromol. Chem., Rapid Commun.* **1984**, *5*, 157−164.
(11) Wernet, W.; Monkenbusch, M.; Wegner, G. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 193−197.
(12) Jönsson, B.; Lindmann, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons: New York, 1998.
(13) Smela, E. *J. Micromech. Microeng.* **1999**, *9*, 1−18.
(14) Bay, L.; Jacobsen, T.; Skaarup, S.; West, K. *J. Phys. Chem. B* **2001**, *105*, 8492−8497.
(15) Paquette, R. G.; Lingafelter, E. C.; Tartar, H. V. *J. Am. Chem. Soc.* **1943**, *65*, 686.
(16) Paquette, R. G.; Lingafelter, E. C.; Tartar, H. V. *Fette Seifen* **1955**, 236.
(17) Cordon, T. C.; Maurer, E. W.; Stirton, A. J. *J. Am. Oil Chem. Soc.* **1970**, *47*, 203.
(18) Swisher, R. D. *J. Am. Oil Chem. Soc.* **1967**, *44*, 717.
(19) Doe, P. H.; El-Emary, M.; Wade, W. H.; Schecter, R. S. *J. Am. Oil Chem. Soc.* **1977**, *54*, 570.
(20) Franses, E. I.; Pulg, J. E.; Talmon, Y.; Miller, W. G.; Scriven, L. E.; Davis, H. T. *J. Phys. Chem.* **1980**, *84*, 1547−56.
(21) van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, 1−9.
(22) Koon, D. W. *Rev. Sci. Instrum.* **1988**, *60*, 271−274.
(23) Benslimane, M.; Gravesen, P.; West, K.; Bay, L.; Skaarup, S. *7th Int. Conf. on New Actuators*, Bremen, Germany, 2000; pp 635−638.
(24) Sauerbrey, G. Z. *Z. Phys.* **1959**, *155*, 206−222.
(25) Diaz, A. F.; Castillo, J. I. *J. Chem. Soc., Chem. Commun.* **1980**, 397−398.
(26) Trinidad, F.; Alonso-Lopez, J.; Nebot, M. *J. Appl. Electrochem.* **1987**, *17*, 215−218.
(27) Rodriguez, J.; Otero, T. F.; Grande, H.; Moliton, J. P.; Moliton, A.; Trigaud, T. *Synth. Met.* **1996**, *76*, 301−303.
(28) Skaarup, S.; West, K.; Gunaratne, L. M. W. K.; Vidanapathirana, K. P.; Careem, M. A. *Solid State Ionics* **2000**, *136−137*, 577−582.
(29) Bay, L.; Skaarup, S.; Vlachopoulos, N.; West, K. *SPIE 8th. Int. Symp. on Smart Struct. Mater.*, Newport Beach, CA, 2001; pp 54−58.
(30) Wynne, K. J.; Street, G. B. *Macromolecules* **1985**, *18*, 2361−2368.
(31) Chiarelli, P.; De Rossi, D.; Dellasanta, A.; Mazzoldi, A. *Polym. Gels Networks* **1994**, *2* (3−4), 289−297.
(32) Spinks, G. M.; Lui, L.; Wallace, G. G.; Zhou, D. Z. *Adv. Funct. Mater.* **2002**, *12* (6−7), 437−440.
(33) Pei, Q.; Inganäs, O. *J. Phys. Chem.* **1992**, *96*, 10507−10514.

MA0207327