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Doping-Induced Strain in Polyaniline: Stretchoelectrochemistry

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Dimensional changes in oriented and unoriented polyaniline induced by protonic acid doping or redox doping have been demonstrated. Sample elongations upon doping are anisotropic in stretch-oriented material, with the greatest expansion in the direction perpendicular to the draw axis. The observed electrochemical/mechanical phenomena are reversible for protonation/deprotonation and for redox cycling, although creep under stress occurs in perpendicular and nonoriented samples under the latter conditions. Limiting elongations are not dependent on the size of the dopant ion, but the rate of protonic doping is slower for larger ions. Electrochemical doping, effected through constant current or constant potential, affords a high degree of control on the rate and extent of dimensional change and occurs with high coulombic efficiency over a range of current densities.

Introduction

Neutral conjugated polymers may be rendered electrically conducting by the introduction of charge carriers.[1,2] This doping process, which takes place during or subsequent to synthesis, involves partial oxidation or reduction of the polymer backbone and can be performed chemically or electrochemically:[3]

$$\text{Pol} + y\text{A}^- \rightarrow \text{Pol(A)}_y + ye^- \qquad \text{oxidation (p-doping)}$$

$$\text{Pol} + ye^- + y\text{D}^+ \rightarrow \text{Pol(D)}_y \qquad \text{reduction (n-doping)}$$

where Pol represents the neutral polymer, and A^- and D^+ are anions and cations, respectively, that are required to maintain electrical neutrality. Doping can also occur via protonation:[4]

$$\text{Pol} + y\text{HA} \rightarrow \text{Pol(H)}_y\text{(A)}_y$$

Although the main focus has been on the very strong dependence of electronic conductivity on doping level, other properties of conducting polymers also change with doping. Since the doping process is often reversible the properties may be controlled to a high degree using electrochemical techniques. Thus, electrochemical transistors,[5] ion gates,[6] and electrochromic devices[7] have been made, employing reversible changes in electronic conductivity, ionic conductivity, and optical density, respectively. One of the consequences of doping is that the polymer must swell to accommodate the counter ion (A^- or D^+ above). Dimensional changes[8,9] following chemical and electrochemical doping have been noted since the onset of research into conjugated polymers[10] and are, for example, responsible for corrugations in the surface of polymer films grown on electrode surfaces.[11] There are other classes of electroactive conducting materials which expand on doping, such as layered chalcogenides[12] and graphite.[13] If measured with adequate sensitivity, dimensional changes can be correlated with discrete phase transitions ("staging").[14] Two-dimensional inorganic materials exhibit highly anisotropic expansion, since ions fit in between planes.

These types of electrochemically induced dimensional changes in materials are distinct from electric-field-induced responses, such as piezoelectricity.[15] Recently, an organic polymer gel that undergoes electric field driven motility was reported.[16] Rheological changes in polymer solutions under an applied voltage gradient ("electrorheology[17]") provide another example of a field-driven response. In the systems discussed below the response is a result of bulk electrochemical activity, and the materials are thus required to be both electronic and ionic conductors. Possible applications of inorganic solids can be compromised by excessive rigidity and brittleness. Polymers offer better mechanical integrity and processibility for many applications. In addition, the extent of molecular chain orientation in polymers can be enhanced by mechanical deformation.[18] Material properties, such as electronic conductivity[19] and bulk modulus,[20] having a

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(1) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

(2) Chien, J. C. W. *Polyacetylene; Chemistry, Physics and Materials Science*; Academic Press: New York, 1984.

(3) MacDiarmid, A. G.; Mammone, R. J.; Krawczyk, J. R.; Porter, S. J. *Mol. Cryst. Liq. Cryst.* **1984,** *105,* 89.

(4) Han, C. C.; Elsenbaumer, R. L. *Proc. 3rd Int. SAMPE, Elect. Conf.* **1989,** 419.

(5) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985,** *89,* 1441.

(6) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982,** *104,* 6139.

(7) Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem.* **1984,** *177,* 281.

(8) Chiarelli, P.; et al. In *Polymer Gels: Fundamentals and Biomedical Applications*; DeRossi, D., Ed.; Plenum Press: New York, 1991; 195.

(9) Aizawa; et al. In ref 8, p 147.

(10) Francois, B.; Mermilliod, N.; Zuppiroli, L. *Synth. Met.* **1981,** *4,* 131.

(11) See Tourillon, G. In ref 1, p 293.

(12) Wittingham, M. S. *Prog. Solid St. Chem.* **1978,** *12,* 41.

(13) Bardhan, K. K.; Chung, D. D. L. *Carbon* **1980** *18,* 313.

(14) Biberacher, W.; Lerf, A.; Besenhard, J. O.; Mohwald, H.; Butz, T. *Mater. Res. Bull.* **1982,** *17,* 1385.

(15) Ikeda, T. *Fundamentals of Piezoelectricity*; Oxford University Press: Oxford, 1990.

(16) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992,** *355,* 242.

(17) Block, H.; Kelly, J. P.; Qin, A.; Watson, T. *Langmuir* **1990,** *6,* 6.

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range of anisotropies may be obtained by stretch alignment of conjugated polymers.

Electrochemical/mechanical relationships in conducting polymers have recently been explored with a view toward the fabrication of novel devices. Microelectrochemical actuators, such as microtweezers and fluid flow controllers, have been proposed by Baughman et al.[21,22,23] The construction of "artificial muscle" was also suggested,[21] where polymers would contract or relax during undoping or doping cycles, respectively. If doping is done electrochemically there is the potential for a very high degree of control in "stretchoelectrochemical" systems. Changes in pH can also be used to effect doping, although there are many examples of synthetic polymer based gels that exhibit very large (isotropic) volume changes in response to pH.[24]

For our studies we decided to use polyaniline[25] as a representative conducting polymer. Our choice was dictated by the facts that polyaniline is easily synthesized, is soluble and therefore processible, is stable to ambient and aqueous environments,[26] may be stretch oriented,[27] and demonstrates reversible electrochemical activity.[28] Furthermore, since the polymer contains a rather basic heteroatom (nitrogen) in the backbone, protonation as a route to doping is facile and occurs under mild conditions.[29] Our goals in this study were thus to determine the extent of dimensional changes in polyaniline upon doping, to probe the reversibility of electrochemistry and strain, and to establish the degree to which these phenomena could be controlled by chain orientation.

Experimental Section

Synthesis of polyaniline in the emeraldine base (EB) form followed the method of MacDiarmid et al.[30] Aniline was polymerized by ammonium persulfate in 1.0 M aqueous HCl at −2 °C using a 4:1 mole ratio of monomer:oxidizer. The resulting emeraldine salt (ES) was neutralized with NH_4OH, dried, and dissolved in *n*-methyl-2-pyrrolidinone (NMP). Films ranging in thickness from 50 to 200 μm were cast from 2% solutions in NMP onto silanized glass. Casting was performed under vacuum at 60 °C. Films of EB were oriented by manual stretch-elongation at 130 °C.

Elongation measurements were performed at room temperature using an in-house-designed device that consisted of a lever arm extending over a Mettler balance from which films could be hung. A micrometer was attached to the center of the lever arm and pressed on the balance pan. A small nylon cup glued around the sample served as a reservoir for electrolytes. The sample protruded below the cup and was clamped to a spring. The weight registered on the balance was related to the change in length of the wetted part of the sample through the spring constant (which was determined separately). The micrometer was used to provide the starting tension on the polymer (50–100 g). Using a spring constant of ca. 10 g/mm and a balance sensitivity of 0.01 g the apparatus is capable of detecting absolute changes in length of 1 μm or relative changes of 0.01%. The assembly was placed in an insulated box to minimize thermally induced drift, which limited relative changes to about 0.1% in practice.

Protonic acid doping was performed with 1.0 M aqueous acids (HCl, $HClO_4$, HF). In cases where undoping through the addition of base was required, the material for the reservoir was Teflon. Typically, the elongation was determined as a function of exposure time, with a positive elongation indicative of expansion.

Electrochemical doping was performed by attaching a thin wire to the nonwetted part of a conducting film and using sulfuric acid as an electrolyte. The counter electrode was lead, which produces a convenient reference potential via the $Pb/PbSO_4$ redox couple. A General Resistance E-35 current source was used to provide constant current, and for controlled-potential experiments, a Princeton Applied Research (PAR) 173 potentiostat was used in conjunction with another lead electrode. The addition of various electrodes was experimentally determined not to affect the spring constant of the apparatus.

Results and Discussion

We were consistently able to obtain draw ratios of 3 using manual stretching of the material prepared as described. The as-cast EB is known to contain some 15% of residual NMP which apparently serves as a plasticizer during stretching.[31] Higher draw ratios have been reported (up to 4.5) using specialized apparatus.[27] Wider samples were required for experiments involving elongation along a direction perpendicular to the draw axis, which limited the draw ratio to 2.5. The modification to the balance described above provided a very convenient and inexpensive setup for measuring dimensional changes in polymer samples. The long-term (hours) drift was less than 0.1% elongation for a 17-mm sample, and the readings were stable to 0.01%. The tension applied to the samples was not enough to cause stretching by itself.

Protonic Acid Doping. Exposure of nascent EB films to aqueous acid, the first cycle of protonic acid doping, caused a *decrease* in the length of the sample. We attribute this to either the release of some stored elastic stress, or to the removal of residual NMP. The sample shown in Figure 1 was subjected to alternating protonation/neutralization cycles using HCl and NaOH. The percent elongation during each cycle is depicted. As can be seen, contraction of the film occurs following the addition of base (and acid on the first cycle). Further cycling leads to reversible dimensional changes. It is apparent that doping (protonation) occurs much more quickly than undoping. If we assume the actual protonation/deprotonation step is fast, the limiting process appears to be permeation of OH^- or H^+ through the film. While hydroxide ions are larger than protons and would be expected to diffuse slower, the rate of permeation depends also on the concentrations of ions within the material. Thus, unprotonated polyaniline, which contains few ions, would exhibit low permeability. This type of behavior

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(18) Bradley, D. D. C.; Friend, R. H.; Lindenberger, H.; Roth, S. *Polymer* **1986**, *27*, 1709.

(19) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1984**, *12*, 293.

(20) Machado, J. M.; Masse, M. A.; Karasz, F. E. *Polymer* **1989** *30*, 1992.

(21) Baughman, R. H.; Shacklette, L. W.; Elsenbaumer, R. L.; Plichta, E.; Becht, C. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, Bredas, J. L., Chance, R. R., Eds.; Kluwer: Netherlands, 1990; p 559.

(22) Baughman, R. H.; Shacklette, L. W. In *Science and Applications of Conducting Polymers*; Salaneck, W. R., Clark, D. T., Samuelson, E. J., Eds.; A. Hilger: New York, 1990 p 47.

(23) Baughman, R. H.; Shacklette, L. W.; Elsenbaumer, R. L.; Plichta, E. J.; Becht, C. In *Molecular Electronics*; Lazarev, P. I., Ed.; Kluwer: Netherlands, 1991; p 267.

(24) Siegel, R. A.; Firestone, B. A. *Macromolecules* **1988**, *21*, 3254.

(25) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.

(26) Angelopoulos, M.; Asturias, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G.; Akhtar, M.; Kiss, Z.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 151.

(27) Cromack, K. R.; Jozefowicz, M. E.; Ginder, J. M.; Epstein, A. J.; McCall, R. P.; Du, G.; Leng, J. M.; Kim, K.; Li, C.; Wang, Z. H.; Druy, M. A.; Glatkowski, P. J.; Scherr, E. M.; MacDiarmid, A. G. *Macromolecules* **1991**, *24*, 4157.

(28) MacDiarmid, A. G.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 187.

(29) Chiang, J.-C., MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.

(30) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein A. J. In *Conducting Polymers*; Reidel: Dordrecht, 1987, p 105.

(31) Wei, Y.; Jang, G.-W.; Hsueh, K.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Polymer* **1992**, *33*, 314.

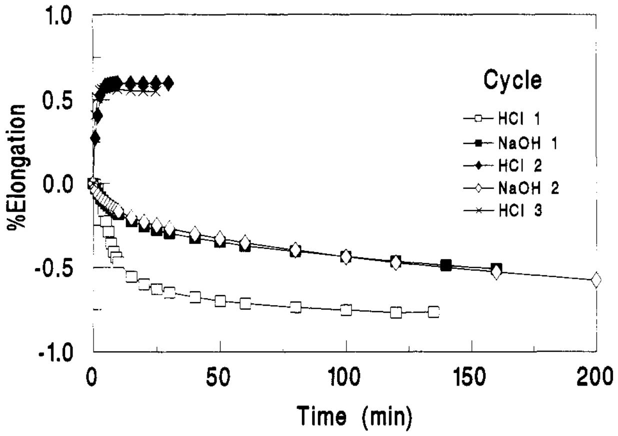

Figure 1. Elongation as a function of time for a parallel-oriented polyaniline film cycled between acid and base. The first cycle is protonation of as-cast emeraldine base.

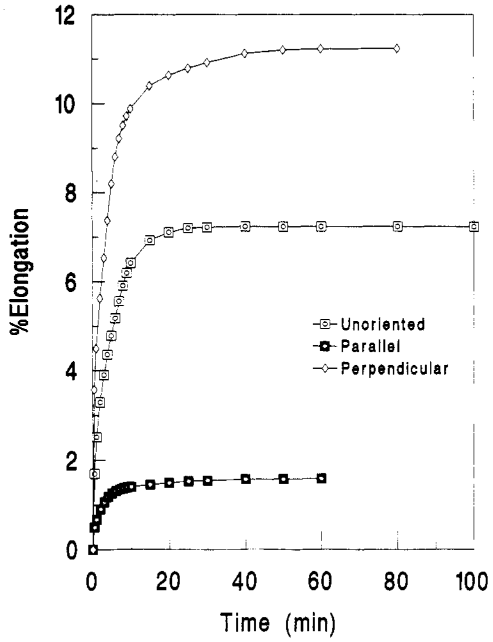

Figure 2. Comparison of the length change upon protonation of stretched emeraldine base films with the measurement direction parallel and perpendicular to the draw axis, and also unstretched. 1 M HCl(aq) used for protonation.

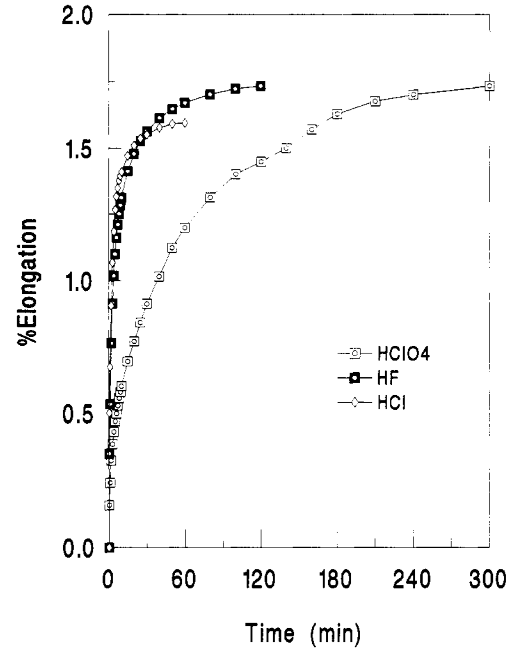

Figure 3. Elongation vs doping time for parallel emeraldine base films using perchloric, hydrofluoric, and hydrochloric acids.

was observed in dense polypyrrole films by Burgmayer and Murray,[32] who varied the ionic content of their materials by electrochemical doping/undoping.

As observed previously,[27] the conductivity of stretched doped polyaniline was found to be anisotropic. For our material, the conductivity of protonated film (ES) was 86 Ω^{-1} cm^{-1} along the draw axis and 13 Ω^{-1} cm^{-1} perpendicular. The conductivity of unstretched ES was 24 Ω^{-1} cm^{-1}.

Strong anisotropy is also observed when elongations of stretched and unstretched EB films are compared. In Figure 2 percent change in length is depicted as a function of doping time for an unoriented sample, and for samples with the measurement direction parallel and perpendicular to the draw axis. Consistent with a zero-order view that dopant counterions should fit in between chains and push them apart, the perpendicular orientation shows much more elongation than the parallel one. The unoriented EB shows intermediate behavior. In a perfectly oriented polyaniline system the only mechanism for sample elongation would be via a lengthening of the bonds or an increase in the dihedral angle between phenyl rings. Structural studies by Pouget et al.[33] on polyaniline indicate that neither of these parameters change significantly. If we reason that any elongation in the parallel sample is due to the projection of residual molecular orientation perpendicular to the stretch axis, the average orientation of molecules can be estimated by $\tan\theta = 1.62/11.1$ (the ratio of the equilibrium swelling lengths). The spreading angle determined thus is $\theta = 8.3°$. For comparison, Cromack et al.[27] determined, from X-ray diffraction, a spreading angle of about 7° in 4-fold drawn undoped polyaniline. Interestingly, the anisotropy ratio in the elongations (6.9) is close to the anisotropy ratio for the conductivity (6.6).

For doping by HCl, no difference in doping rate between stretched and unstretched films was noted. However, doping with perchloric acid occurs much more slowly than with HCl or HF, as shown in Figure 3. The process is pseudo-Fickian diffusion, as illustrated by the linearity of the early portion of an elongation vs $t^{1/2}$ plot (Figure 4). There is also no significant difference in limiting elongations (obtained at long times) when comparing different counterions. Assuming the dimensional changes are proportional to the amount of doping, diffusion coefficients in these ca. 100-μm-thick films were estimated using the following equation, valid for short times:[34,35]

$$f = 4D^{1/2}t^{1/2}/\pi^{1/2}h$$

where f = observed elongation at time t/final elongation, D is the diffusion coefficient, and h the thickness of the film. Diffusion coefficients for Cl$^-$, F$^-$, and ClO$_4^-$ are ca. 4×10^{-8}, 3×10^{-8}, and 2×10^{-9} cm^2 s^{-1}, respectively. The result that the larger perchlorate ion diffuses more slowly

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(32) Burgmayer, P.; Murray, R. W. *J. Phys. Chem.* **1984**, *88*, 2515.

(33) Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* **1991**, *24*, 779.

(34) Jost, W. *Diffusion in Solids, Liquids, and Gases*; Academic Press: New York, 1960; pp 37, 45.

(35) Schlenoff, J. B.; Chien, J. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 6269.

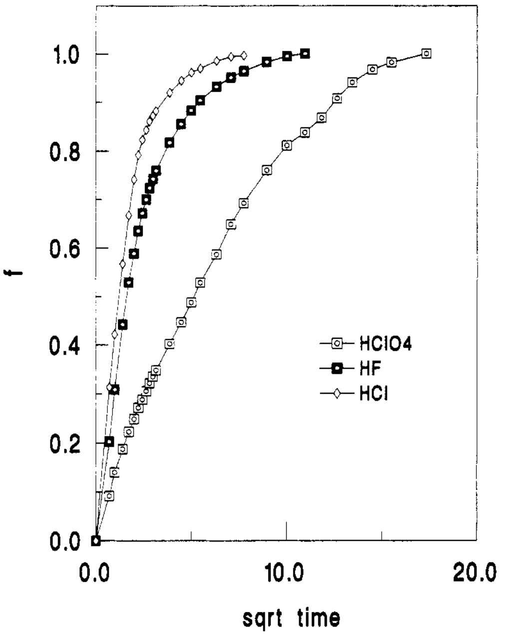

Figure 4. Fraction of elongation versus $t^{1/2}$ for protonic acid doping of stretched emeraldine base as in Figure 3, showing approximately linear behavior at $f < 0.7$.

is reasonable, but the finding that the limiting dimensional change for the three ions is similar is unexpected. Pouget et al.[33] note that the expansion of the unit cell of EB upon protonation is considerably larger than the volume of the chloride counterions, a curious result confirmed by small-angle X-ray scattering.[36] It is likely that significant coinsertion of solvent occurs with doping,[37] and the solvent occupies the unaccounted-for volume.

Electrochemical Doping. Stretched and unstretched EB films were converted to ES using HCl and dried prior to attachment of electrical contacts. Sulfuric acid (0.5 M) was used as the electrolyte and electrochemistry thus involved protonated forms of the various redox states of polyaniline. As made, polyaniline is at the 50% oxidation level (doping level, y, of 0.5), which corresponds to an equal mixture of pernigraniline (completely oxidized, $y = 1.0$) and leucoemeraldine (completely reduced, $y = 0.0$).[25] The first electrochemical cycle was uniformly chosen to be reduction for several reasons. First, we found rapid mechanical failure even for a small amount of doping above the 0.5 level. Second, MacDiarmid et al.[38] have found that protonation of pernigraniline does not occur under the conditions used and attack by the (weakly nucleophilic) counterion on the phenyl ring occurs instead. Further, Stilwell and Park[39] showed that polyaniline undergoes hydrolysis to benzophenone at high potentials. We found that reduction to a level below about $y = 0.3$ at our current density (typcially around 0.5 mA for a 17 mm × 4 mm × 0.1 mm sample) led to a material that was sufficiently nonconductive that it could not sustain the current imposed by the current source. In our constant-current experiments we typically used a 2-h charge/discharge rate (0.077 A g^{-1}) and passed current for 30 min.

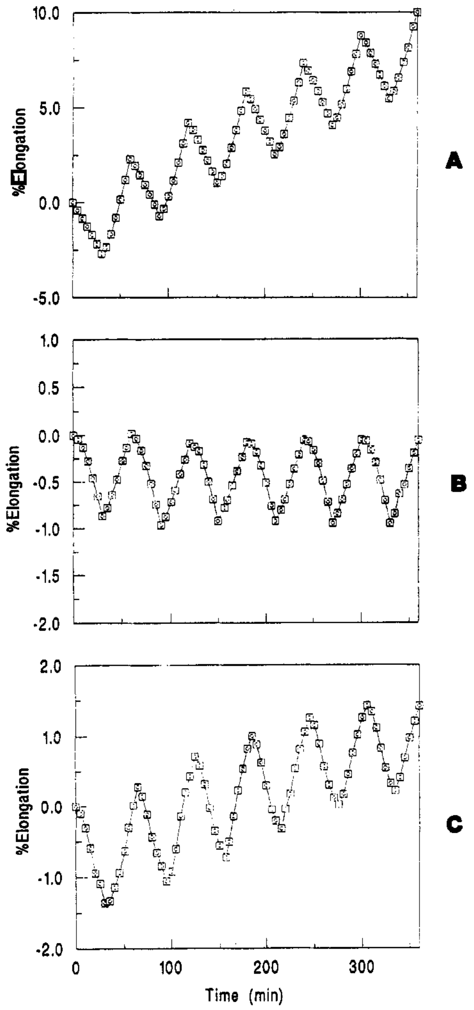

Figure 5. Elongation vs time for electrochemical doping/undoping cycles of (a) perpendicular, (b) parallel, (c) unoriented polyaniline in 0.5 M sulfuric acid. Each polarity of redox activity lasts for 30 min and is performed at a 2-h rate of charge/discharge (or 0.077 A g^{-1}). Negative-going elongation corresponds to reduction.

Electrochemical doping can be done via constant current or constant potential. The former method has the advantage that the rate of oxidation/reduction is controlled by the current. Figure 5 depicts elongation vs time for several consecutive reduction/oxidation cycles of stretched and unstretched polyaniline. Each 60-min cycle corresponds to a change in doping level of $y = 0.50$ to 0.375 and back. Behavior similar to that observed in the proton doping case is evident, in that the polymer contracts when the ionic content is decreased through undoping. The magnitude of dimensional change is somewhat smaller, since undoping could not be carried to completion. Elongation on doping is greatest for the direction perpendicular to the draw axis and least for parallel. Unstretched films show intermediate behavior. The linearity of each dimension vs time cycle implies that elongation is, indeed, proportional to doping level. If the response of each film is given in terms of an electrochemical "expansion coefficient" or percent elongation vs doping level change, $\% e/\Delta y$, we can estimate the following values for parallel, perpendicular, and unoriented polyaniline: 7.1, 27.0, 11.3. The spreading angle estimated from the dimensional anisotropy is $\tan \theta = 7.1/27$, $\theta = 15°$.

A significant observation was that both the perpendicular and (to a lesser extent) unoriented films exhibited

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[36] Annis, B. K.; Lin, J. S.; Scherr, E. M.; MacDiarmid, A. G. *Macromolecules* **1992**, *25*, 429.

[37] Okabayashi, K.; Goto, F.; Abe, K.; Yoshida, T. *Synth. Met.* **1987**, *18*, 365.

[38] MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Weiss, H.; Epstein, A. J. *Synth. Met.* **1991**, *41*, 621.

[39] Stilwell, D. E.; Park, S.-M. *J. Electrochem. Soc.* **1989**, *136*, 688.

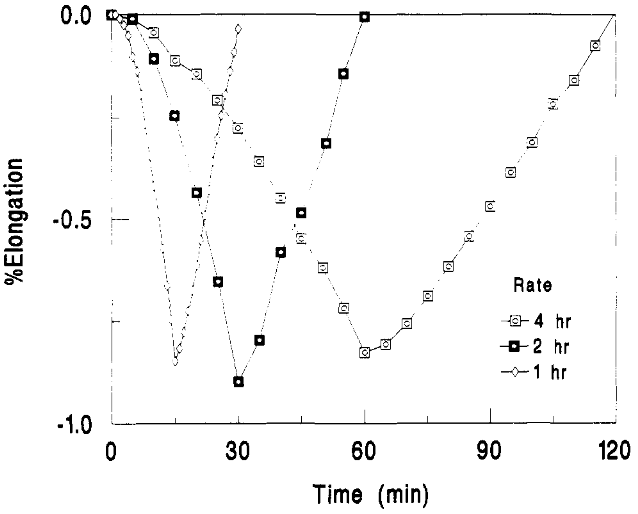

Figure 6. Elongation vs time for one electrochemical reduction/oxidation cycle of parallel oriented polyaniline at current densities corresponding to a 4-, 2-, and 1-h rate.

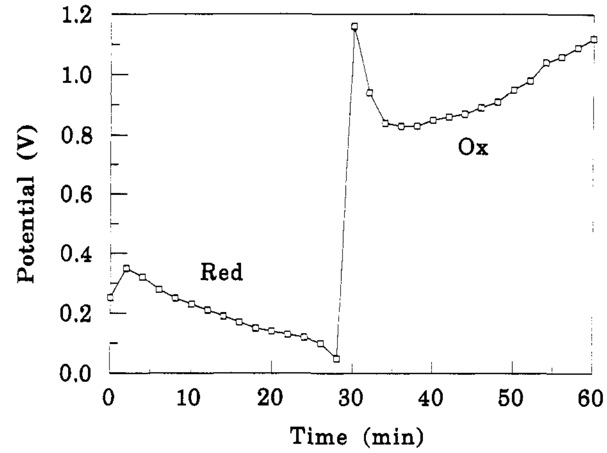

Figure 7. Potential, measured vs a Pb/PbSO$_4$ reference, as a function of time for parallel oriented polyaniline in 0.5 M H$_2$SO$_4$ *under constant current cycling at a 2-h rate. Polymer is initially* in the emeraldine oxidation state.

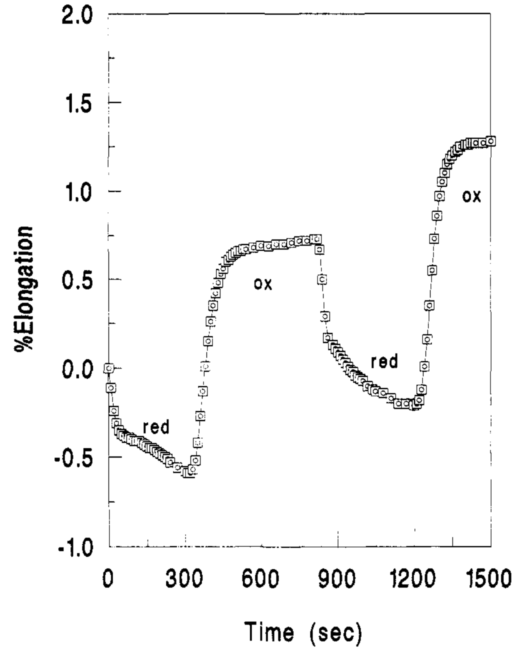

Figure 8. Elongation as a function of time for parallel oriented polyaniline in response to potential stepping between 0.55 (red) and 1.10 V (ox) vs Pb/PbSO$_4$ in 0.5 M H$_2$SO$_4$.

creep: on reoxidation the length of the sample was greater than the length at the start of the cycle. For example, in the perpendicular films the elongation on the oxidation cycle was almost double the contraction on the reduction cycle. In contrast, parallel samples exhibited excellent repeatability (Figure 5b). It is possible that the movement of ions through the polymer, coupled with structural changes, allow the molecules to slide past one another under the (small) tensioning load of 10 kg cm^{-2}. (We did not perform a detailed study of the effect of tensioning on creep.) This behavior ultimately places a practical limitation on the use of polyaniline in electrochemical–mechanical applications where the polymer is under strain. Parallel oriented film may be employed, but the dimensional changes are, unfortunately, the lowest.

The degree of control over the rate of elongation is illustrated in Figure 6, which depicts change in dimension vs time for current densities corresponding to a 1-, 2-, and 4-h rate (0.15, 0.077, and 0.036 A g^{-1}, respectively). In all cases the current polarity is switched after the doping level has gone from 0.50 to 0.375. Samples reach similar percent elongations at the end of the reduction stage and return to the same length as at the start of the cycle. Both of these findings indicate that the Coulombic efficiency for the cycling is high. In other words, charge passed during cycling leads to redox reaction on the polyaniline and is not consumed in side reactions such as solvent oxidation/reduction.

The potential of the polyaniline in response to constant applied current is shown in Figure 7, with lead sulfate as the reference electrode. The equilibrium potential of y = 0.50 polyaniline is about 0.6 V, and approximately 0.2 V of overpotential is required to pass 0.077 A g^{-1} current of either polarity. If the response of polyaniline in controlled potential is to be reversible, precisely the right potential must be applied on oxidation and reduction to avoid composition drift during multiple cycling. For example, Figure 8 shows the response of a sample under applied potential stepping between 0.55 and 1.10 V vs PbSO$_4$. The oxidative potential (1.10 V) is considerably more removed from the equilibrium potential than is the reduction step. The result is that the composition drifts toward the pernigraniline (fully oxidized) state after each cycle. For reversible behavior the constant-current mode is better, unless the shortest possible response time is required.

In summary, dimensional changes in oriented and unoriented polyaniline resulting from protonic or redox doping have been measured. The process is largely reversible. Elongation upon doping is anisotropic in oriented films using either method of doping. Electrochemical cycling shows high Coulombic efficiency, although the only system that shows dimensional reversibility is the parallel orientation. Creep under tension is observed in the electrochemical cycling of unoriented and perpendicular polymer.

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