

Decay of Electrical Conductivity in *p*-Toluene Sulfonate Doped Polypyrrole Films

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Abstract: Long term performance of conductivity of *p*-toluene sulfonic acid (pTSA) doped electrochemically synthesized polypyrrole (PPy) films was estimated from accelerated aging studies between 80°C and 120°C. Conductivity decay experiments indicated that overall aging behavior of PPy films deviated from first order kinetics at prolonged aging times at elevated temperatures. However, an approximate value for the activation energy of the conductivity decay of PPy was calculated as $E=47.4$ kJ/mol, enabling an estimate of a rate constant of $k=8.35\times 10^{-6}$ /min at 20°C. The rate of decrease of conductivity was not only temperature dependent but also influenced by the dopant concentration. A concentration of 0.005 M pTSA in the electrolyte resulted in a conductive film and when this film was exposed to 120°C for a period of 40 h, the conductivity decayed to about 1/20 of its original value. The concentration of pTSA was increased to 0.05 mol/l and when the resulting film was aged in the same way, it showed a decrease in the conductivity to about 1/3 of its original value. Both microwave transmission and dc conductivity data revealed that highly doped films were considerably more electrically stable than lightly doped films. The dopant had a preserving effect on the electrical properties of PPy.

Keywords: Polymer, Thin film, Electrochemical technique, Electrical conductivity

Introduction

Conducting polymers can be electrochemically or chemically synthesized with a wide range of electrical conductivities. Stability of electrical properties is an important concern for practical applications. Among intrinsically conducting polymers (ICP), polypyrrole (PPy) films in their oxidized, conducting form possess reasonably good electrical stability in air at room temperature [1,2]. In electrochemical synthesis, simultaneous oxidation and polymerization of the pyrrole monomer occurs at anode, giving rise to an oxidized polymer with a delocalized positive charge on the conjugated π -bond system.

Stability of the electrical conductivity of galvanostatically synthesized conducting polypyrrole (PPy) films and PVC/PPy composites in ambient air at room temperature, doped with different counter ions has been studied [3]. Polypyrrole doped with the organic counter ion *p*-toluene sulfonate (pTSA) was found to exhibit better stability than those doped with inorganic dopants such as ClO_4^- , BF_4^- and NO_3^- . The degradation rate constants were calculated assuming first order kinetics. The degradation of conductivity of PPy/pTSA system was stated to obey first order kinetics with activation energy of 15 kcal/mol, whereas ClO_4^- and BF_4^- anions were observed to give rise to multiorde kinetics in conductivity decay [4]. It was suggested that the degradation mechanism of PPy/pTSA was due to the reaction of oxygen with polymer backbone [4,5]. In the absence of oxygen polypyrrole was found to be stable [6]. In a study of thermal stability of polypyrrole, polymers doped with aromatic anions such as *p*-toluene sulfonate (*p*-TS) and *p*-chlorobenzene

sulfonate (CBS) were found to be more stable than polymers doped with an aliphatic anion, dodecyl sulfate (DDS) [7]. In contrast to the results presented by Samuelson and Druy [4], degradation of conductivity for PPy/pTSA, PPy/CBs and PPy/DDS indicated a non-linear relationship between the natural logarithm of normalized conductivity versus aging time, suggesting a multi-order degradation process. A diffusion-controlled kinetics was suggested to explain the decay of conductivity [7].

Electrical conductivity of electrochemically prepared polypyrrole was found to have a slower degradation rate than that of the chemically polymerized PPy [6]. The reduced stability of the chemically synthesized PPy was attributed to the Cl^- dopant ions, which are attached to the PPy chain with covalent bonds, thus disrupting the conjugation. The C-Cl bonds were thought to act as electron traps, which decreased the mean free path of the charge carriers along the polymer chains. Another possible reason for the observed difference was suggested as the oxidative mechanism being more active on the larger specific area of the chemically polymerised PPy resulting in faster decline of electrical conductivity. The variation of electrical conductivity of chemically synthesized PPy over a period of one hour was also found to obey first order kinetics with activation energy of 46 kJ/mol [8]. However, one-hour aging experiments may not sufficient for a proper assessment of the aging behavior of PPy. Conversely, it has been observed that at longer times the data deviated from the straight line, revealing multi-order degradation kinetics [7,9]. It has also been reported that high temperature aging of PPy coated textiles followed a multi-order kinetics. The conductivity loss was reported to proceed through two stages. The initial stage of conductivity decay was thought to follow a diffusion-controlled kinetics,

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where the diffusion of the oxygen into the polymer was the rate-limiting factor [7].

In this work the conductivity decay process in air of pTSA doped PPy films and the effect of the dopant anion concentration on the degradation process were investigated.

Experimental

Polypyrrole films were galvanostatically synthesized in a one-compartment cell. The pyrrole concentration was 0.2 mol/l in aqueous solution. PPy films were lightly and highly doped with *p*-toluene sulfonate with concentrations of 0.005 mol/l and 0.05 mol/l respectively with the latter concentration resulting in a highly conductive film. Galvanostatic synthesis was carried out at a current density of 1.5 mA/cm² for a period of one hour at room temperature. The films were peeled off the stainless steel anode, washed with distilled water and dried prior to conductivity measurements.

Conductivity measurements were performed by using a four probe. A current of 1 mA was supplied to outer electrodes and the corresponding potential drop across the inner electrodes was stored by a data-logger at one-minute intervals. The conductivity measurements on polypyrrole samples were performed at fixed temperatures of 80 °C, 100 °C and 120 °C as a function of time. Conductivity data was normalized and plotted with respect to aging time.

Results and Discussion

Conductivity of polypyrrole increased with temperature similar to that of amorphous semiconductors. A temperature dependent conductivity increase at 80 °C, 100 °C and 120 °C followed by decay in conductivity can be seen in Figure 1. The rate of decay increased with the temperature.

The data in Figure 1 suggests that the decay process following the maximum in conductivity is complex and this is plotted in linear time coordinates in Figure 2. The degradation pattern is similar to that observed by Truong *et*

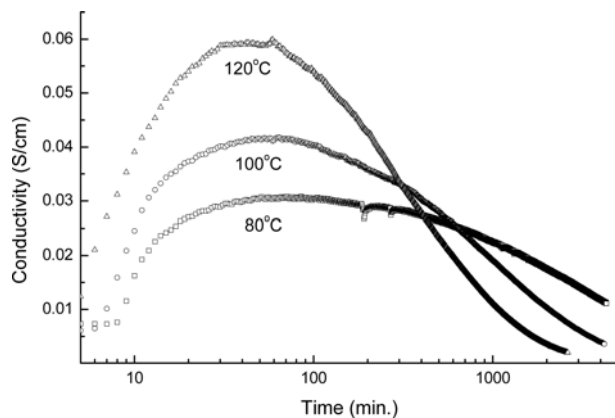


Figure 1. Electrical conductivity versus aging time for lightly pTSA doped PPy film at 80 °C, 100 °C, and 120 °C.

al. [7], where films follow two regions; a rapid decline followed by an exponential decay (Figures 2 and 3). An exponential curve fit describes the decay behavior well during the second part of degradation, starting from about 800 minutes, lasting to the end of the aging experiment, suggesting that two different mechanisms taking place during the degradation of PPy films. While this trend does not accord with some results [4,8] presented in literature, there is agreement with the observations by Truong *et al.* [7].

The loss of conductivity at both elevated temperatures and at room temperature with time could not simply be attributed to oxidation of the main PPy chain. Although, the degradation behavior could not be exactly represented by the first order kinetics, linear fits to natural log of normalized conductivity were performed (Figure 3) to make approximate predictions of electrical lifetime of conducting polypyrrole films. Estimates of the degradation rate constant, *k* can be made from the following equation:

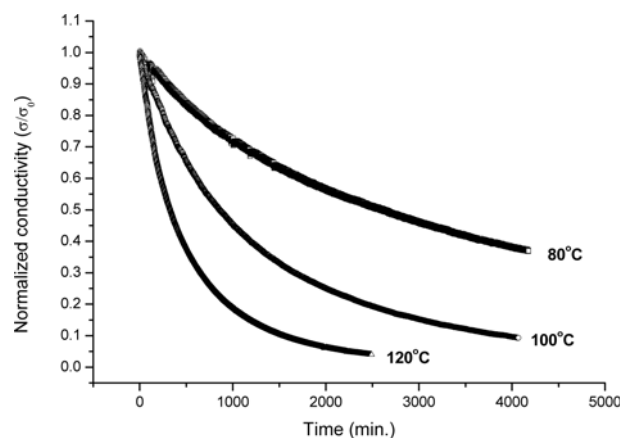


Figure 2. Normalized conductivity versus time of lightly doped polypyrrole films (0.005 mol/l pTSA).

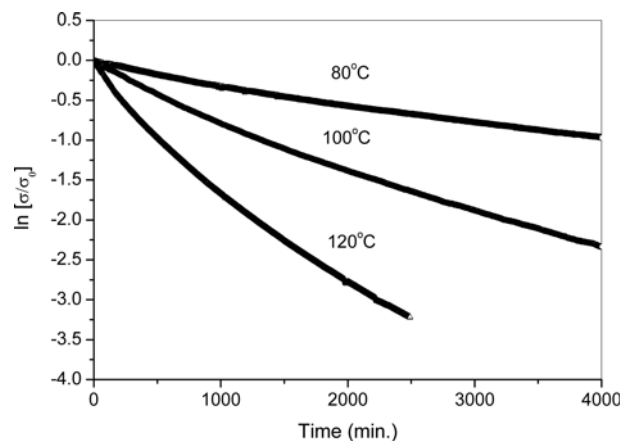


Figure 3. Natural logarithm of normalized conductivity versus time (minutes) of lightly doped PPy films (0.005 mol/l pTSA).

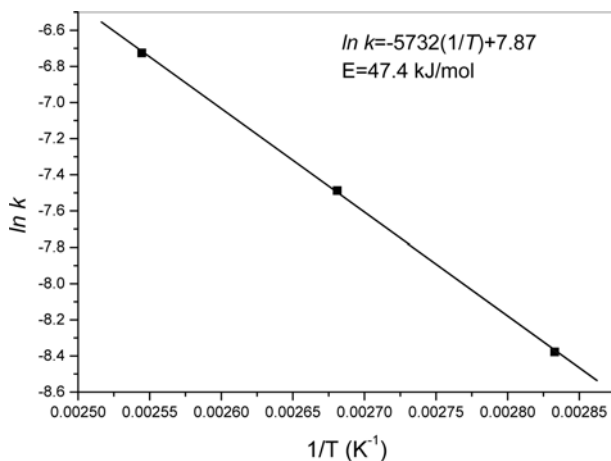


Figure 4. Determination of the activation energy from the graph of $\ln k$ vs. $1/T$ (K^{-1}).

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -kt \quad (1)$$

where σ and σ_0 are electrical conductivities at time t and at the beginning of decay of conductivity respectively.

It was noted in Figure 3 that k increased with temperature and Arrhenius formula was used to obtain the activation energy.

$$\ln k = -\frac{E}{RT} + \ln A \quad (2)$$

where E is the activation energy of the reaction in kJ/mol and the gas constant R is 0.0083 kJ/mol.K. This was shown in Figure 4 which followed equation (3).

$$\ln k = -5732\left[\frac{1}{T}\right] + 7.87 \quad (3)$$

Hence the activation energy of the conductivity decay and the decay constant at room temperature ($T=293$ K) were calculated as $E=47.4$ kJ/mol and $k=8.35 \times 10^{-6}$ /min respectively. The electrical decay at 20°C in an aging period of one year was estimated as $\sigma=0.013\sigma_0$. This was in reasonably good agreement with the conductivity decay data taken from a lightly *p*-TSA doped (0.005M/l) PPy sample, the conductivity of which reduced from about 0.03 S/cm to 0.001 S/cm when exposed to air at room temperature over a period of one year (i.e. $\sigma/\sigma_0=0.033$). However, this estimate is applicable to the polymer dopant system investigated here and individual electrical decay experiments should be performed for other polymer dopant systems with specified synthesis methods and conditions.

It has been observed that the type of the dopant [3,4,6] used had an influence in the degradation behavior of polypyrrole. However, there have been no reports on the effect of the concentration of the dopant on the electrical decay pattern. Earlier experiments by the authors on aging of PPy films at room temperature exposed to air indicated that

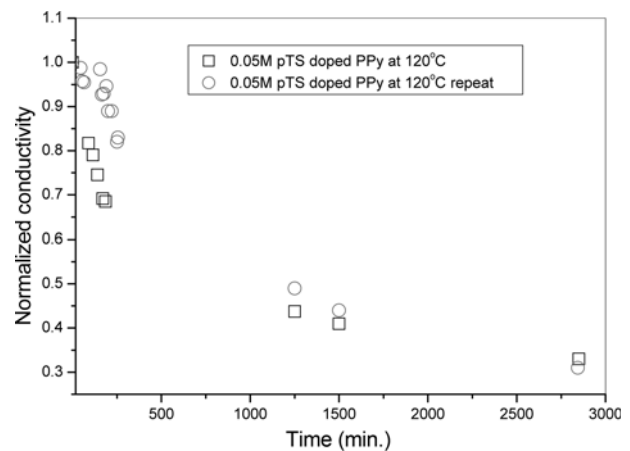


Figure 5. Conductivity decay of highly pTSA doped PPy (0.05 mol/l pTSA).

highly doped PPy (0.1 M pTSA) with an initial conductivity of around 50 S/cm were more stable with a small loss of conductivity compared to that of lightly doped PPy film with an initial conductivity of around 0.01 S/cm [1].

Conductivity loss as a function of time in two consecutive experiments on highly doped (0.05 mol/l) films was plotted in Figure 5. The discrepancy in the two decay patterns in Figure 4 may be attributed to variations caused by factors such as fluctuations in the current, room temperature, inhomogeneous mixing during synthesis and surface morphological variations of the resulting films. When the data in Figures 2 and 5 are compared, it can be seen that the degradation rate was strongly dependent on the concentration of the pTSA. For example, when both the samples at two different dopant concentrations were aged 120°C for a period of 2500 min, the conductivity of the lightly doped sample decayed to about 1/20 of its original value, whereas the conductivity of the sample containing higher concentration of the dopant reduced to about 1/3 of the original value (Figures 2 and 5). Para toluene sulfonic acid had a stabilizing effect on the conductivity of polypyrrole. Moreover, the concentration of the dopant had an effect on the rate of degradation. These observations were also supported by our microwave results, which clearly differentiated the aging behavior of highly and lightly doped films [10]. Microwave transmission, reflection and absorption studies showed that highly doped (0.05-0.1 mol/l pTSA) films retained their high microwave reflectivity whereas lightly doped PPy films (0.005 mol/l) were less stable with a significant increase in the transmission over an aging period of one year. Moreover, our latest studies on microwave properties of flexible substrates coated by pTSA doped PPy by chemical polymerization methods indicated that samples with longer polymerization times and/or higher pTSA concentration had higher electromagnetic shielding effectiveness and better stability of electromagnetic properties than lightly doped

samples and/or samples with short polymerization times [11]. The PPy-pTSA coated samples doped with a concentration of 0.015 mol/l pTSA in the reaction vessel had a 36 % and 27 % decrease in total transmission loss for the 60 and 180 minutes polymerization times respectively. The same values for more highly doped samples (0.027 mol/l pTSA) were 33 % and 16.5 % for 60 and 180 minutes polymerization times respectively.

Although intrinsically conducting polymers have wide ranging modulation of conductivity, their applications are limited due to electrical stability issues, which can be improved to a certain extent by optimization of the reaction parameters, choice and concentration of the dopants. An investigation of the electrical aging characteristics of each conducting polymer system is essential before attempting to use these materials for specific applications.

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