

Aging Studies on Conducting Polypyrrole

Akif Kaynak*

School of Engineering and Technology, Deakin University, Geelong, Victoria 3217, Australia

(Received October 22, 2001; Revised December 4, 2001; Accepted December 10, 2001)

Abstract: Change of tensile properties, electrical conductivity and microwave shielding of electrochemically synthesized polypyrrole films with time are presented. Highly doped films had good electrical stability, retaining high microwave reflectivity throughout the aging period. Lightly doped films were less stable and partially reflective and absorptive of microwaves. FT-IR spectral observations revealed a progressive increase in intensity of an unsaturated conjugated carbonyl peak, which was not observed in the highly doped films, suggesting that the concentration of the dopant had an influence on the mechanism of degradation of conductivity.

Keywords: Polypyrrole, Electrical, Mechanical, Microwave, FTIR spectroscopy

Introduction

Polypyrrole (PPy) is the most frequently used member of conducting polymers. Like other conducting polymers it has an important option of wide range of modulation of its electrical properties. Polypyrrole (PPy) formed electrochemically is a black flexible film, with thickness usually less than 100 μ , has a smooth and shiny surface on the electrode side and a rough, nodular surface on the solution side where growth occurs. The surface roughness of PPy films is sensitive to changes in the electrochemical synthesis conditions[1]. Although more stable than other intrinsically conducting polymers, PPy still suffers from a gradual decline of its mechanical and electrical properties, the knowledge of which is of prime importance for the potential applications of the material.

In this paper, change of tensile properties, electrical conductivity, electromagnetic shielding effectiveness and microwave transmission with time of electrochemically synthesized polypyrrole films are presented. Stability of electrical and microwave properties and some spectral observations are discussed.

Experimental

PPy films were prepared by galvanostatic electrochemical synthesis. Two types of films were synthesized with 0.05 and 0.005 mol/l p-toluenesulphonate (pTS) dopant concentrations with a pyrrole concentration of 0.2 mol/l resulting in high (about 50 S/cm) and low conductivity (about 0.02 S/cm) films respectively. The electrolyte was stirred during the polymerisation and purged with nitrogen. A current density of 1.5 mA/cm² was supplied from a DC current source. Synthesis was carried out for 60 minutes and the deposited film is peeled off the stainless steel anode surface, washed, dried and stored for characterization. Film thickness were in the range of 50-70 microns.

Tensile testing was done by a LLOYD LS 500 machine. A crosshead speed of 2 mm/min and a 200 N load cell were used during experiments.

Electrical conductivity measurements were done by a modified version of the four-probe given in the ASTM D 4496-87. In this technique a small current ranging from 10 μ A to 5 mA is applied to the outer electrodes of the four probe, which is in contact with a rectangular stripe of PPy film of known width and thickness and the voltage drop is measured between the inner electrodes.

Microwave experiments were done by placing the polymer film between two rectangular wave-guides and irradiating with microwaves centered at 10 GHz with a bandwidth of 1 GHz. The interaction of the incident wave with the polymer film in the wave-guide results in a reflected wave (S_{11}) and a transmitted wave (S_{21}), which are measured by a network analyzer. The experimental set up included an HP 8757 C Hewlett Packard Scalar Network Analyzer used in conjunction with an HP 8350 B sweep oscillator, HP 11667A power splitter, HP 85027 E directional bridge, detectors HP 11664 A/E and rectangular wave-guides operating in the frequency range of 8 to 12 GHz. A two-port measurement calibration was performed using precision standards such as open, short, load and a transmission line, removing the effects systematic errors due to frequency response, leakage and mismatch from the measurements.

Infrared reflectance measurements on polypyrrole films were performed using an i-series microscope attached to a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Measurements were taken from 3 different spots on the glossy side of each sample in order to maximize the contribution from specular reflectance. The spectra were obtained from specific coordinates in order to study the aging effects on selected spots. The reflectance spectra were transformed to absorbance by the Kramers-Kronig transformations.

A Jeol JSM-35CF scanning microscope was used for the surface morphology and fracture surface analysis of polypyrrole films. As the samples are conductive, it was not necessary to coat them with gold.

*Corresponding author: akaynak@deakin.edu.au

Results and Discussion

Mechanical Properties

There have been some studies on the mechanical properties of electrochemically synthesized conducting polypyrrole films[2-6] on the effect of synthesis parameters on the tensile properties of these films. Changes in the synthesis parameters have been found to affect the physical properties of the PPy films. For example, surface roughness of PPy films increased with the increase in the current density[7]. A similar observation was reported, in which higher current densities, particularly at values above 5 mA/cm² yielded brittle films with rough surface morphology[2]. Decrease in the current density resulted in smoother films with improved mechanical properties in PPy/pTS films[8]. Breaking stress was reported to decrease with the increase in electrode potential and current density during the electrochemical synthesis[7]. The increase in flotation density of the films with the increase in electrode potential suggested a more open and hence a weaker structure, resulting in lower breaking stress. In another study, the decrease in the synthesis temperature was found to give rise to increase in the breaking strain[3].

Knowledge of change of mechanical properties of PPy films with synthesis parameters and aging time assumes particular importance for applications requiring good mechanical properties and stability of these properties. In this section effects of dopant concentration and aging time on the tensile properties of PPy films are presented. Breaking stress and modulus increased reaching a plateau after about 2 months of aging (Figures 1, 2, and 3) whereas breaking strain decreased with time, initially rapidly and then continued to decrease at a slower rate. This initial rapid embrittlement of PPy films is attributed to the loss of solvent. A similar observation was reported[2] on the effects of water and acetonitrile on the mechanical properties of PPy/pTS. Both acetonitrile and water had significant

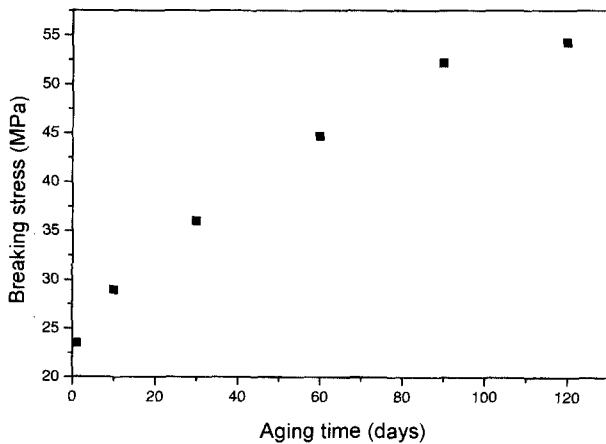


Figure 1. Change of breaking stress with time of PPy films (0.05 M/lt p-TS).

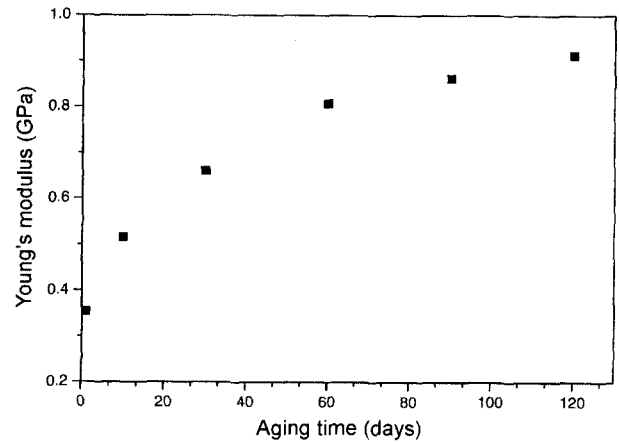


Figure 2. Change of Young's modulus with time of PPy films (0.05 M/lt p-TS).

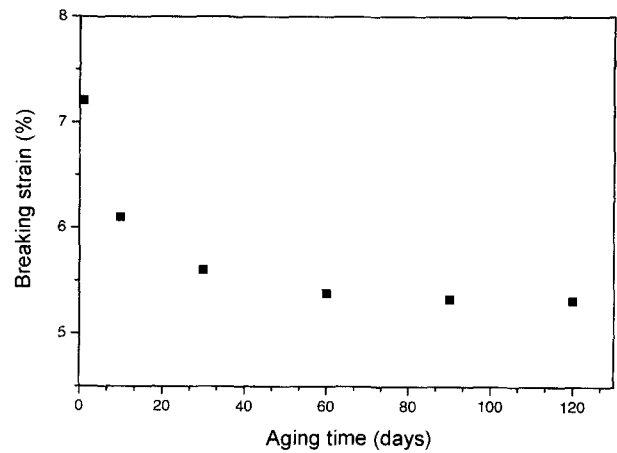


Figure 3. Change of breaking strain with time of PPy films (0.05 M/lt p-TS).

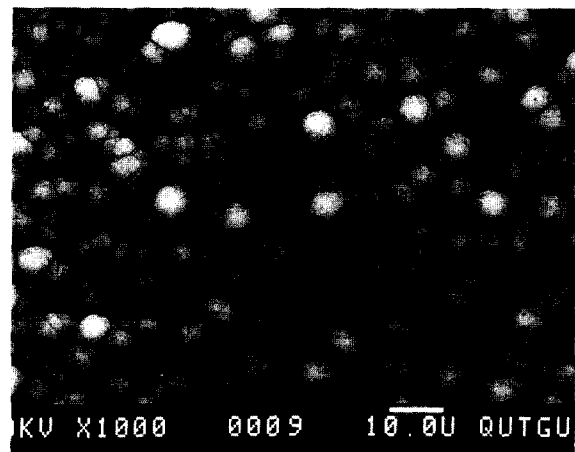


Figure 4. SEM micrograph of a lightly pTS doped (0.005 M/lt p-TS) film synthesized at room temperature for 1 hour. Magnification 1000X.



Figure 5. SEM micrograph of a highly pTS doped (0.05 M/l p-TS) film synthesized at room temperature for 1 hour. Magnification 1000X.

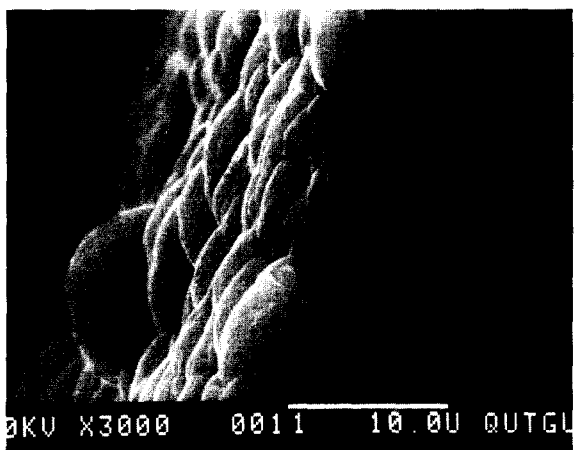


Figure 6. SEM micrograph of fracture surface of the lightly doped film at 3000X magnification.

plasticizing effects on PPy/pTS films by reducing the modulus and tensile strength and increasing elongation at break.

AFM and SEM studies have shown that surface roughness of these films is influenced by pH[9], synthesis time, temperature, dopant type and concentration[1]. For example, lightly pTS doped films had smoother surface morphology with a mean nodule height as low as 500 Å (Figure 4 and Figure 6), whereas highly doped films had rough surfaces with the average nodule height reaching several microns (Figure 5 and Figure 7). SEM micrographs of cross-sections PPy films indicated that the crack path followed the nodule boundaries in the highly doped films, revealing the outline of the nodules at the cross section. Figure 7 shows hollow areas on the fracture surface, indicating that crack propagated around the nodules. In contrast, the cross sections of lightly

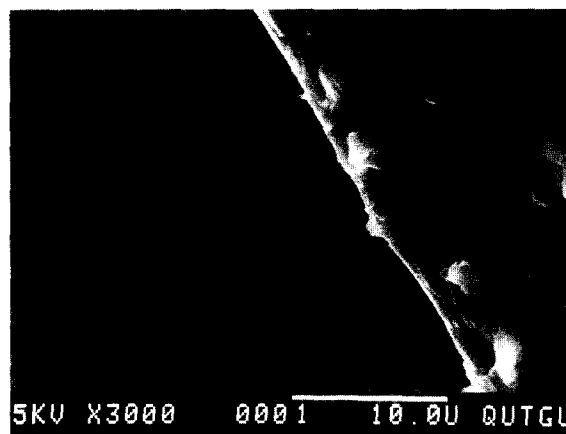


Figure 7. SEM micrograph of fracture surface of the highly doped film at 2000X magnification.

doped films appeared smooth and featureless (Figure 6). A similar observation was made in an examination of fracture surfaces of tensile tested polypyrrole films showing that nodule boundaries are points of weakness facilitating crack propagation[6].

Electrical Conductivity

For a polymer to be conductive two structural features must be present; the existence of double bond conjugation, which provides an orbital system for the carriers to be mobile and introduction of charge carriers extrinsically by a process called "doping"[10]. A controlled variation of electrical conductivity over several orders of magnitude is possible through the doping process. The variation of conductivity of PPy with temperature is similar to that of amorphous semiconductors, increasing with the increase in temperature[11]. Electrical conductivity of polypyrrole films increases not only with temperature but with the concentration of the dopant anion as well, reaching saturation at high doping levels of about 0.05 M/l pTS[12].

The concentration of the dopant anion was observed to have an influence on the stability of conductivity and the kinetics of degradation of conductivity of polypyrrole during aging. The conductivity of the highly doped film was more stable with a lower rate of loss of conductivity compared to that of the lightly doped films. Highly doped films exhibited a loss of about 20% of the initial value whereas lightly doped films had a significant loss of conductivity of about 80% after being exposed to air at room temperature for one year.

The logarithms of conductivity versus aging time is a linear plot in the case of highly doped films (Figure 8) with the degradation rate constant k of $8.36 \times 10^{-9} \text{ sec}^{-1}$. Thus, the degradation of conductivity of highly doped PPy/pTS when exposed to air at room temperature appears to follow first-order degradation kinetics. This suggests that degradation is taking place through reaction of the polymer backbone with

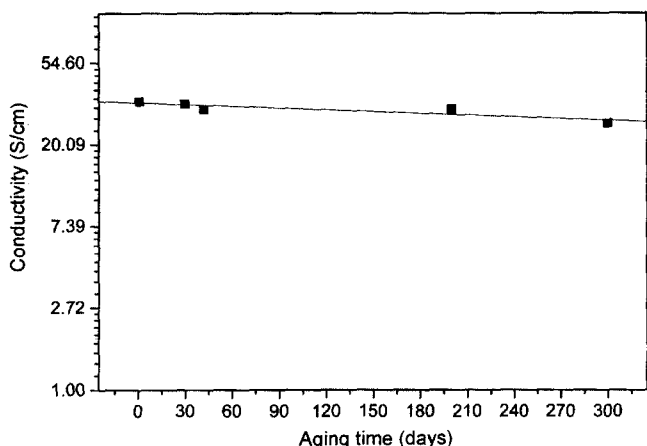


Figure 8. In conductivity vs. aging time of highly doped polypyrrole film.

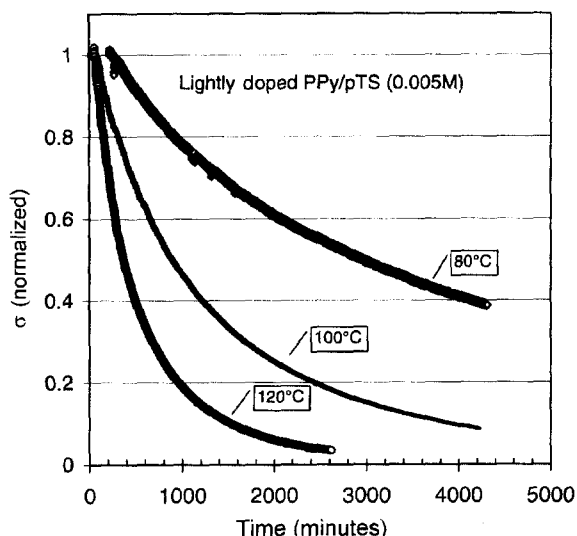


Figure 9. Normalized conductivity vs. time (minutes) of lightly doped PPy/pTS (0.005 mol/lit).

oxygen, which results in formation of carbonyl groups.

Degradation of conductivity of lightly doped PPy films at elevated temperatures can be seen in Figures 9 and 10. The general trend in the plots of normalized conductivity versus aging time for lightly doped (0.005 mol/lit pTS) polypyrrole films at 80°C, 100°C, and 120°C in Figure 9 is that the rate of decay increases with temperature. The deviation of the plots of natural logarithm of normalized conductivity versus aging time from straight line indicated that, in contrast to some data reported in literature[13,14], overall aging behaviour of lightly p-TS doped PPy films at elevated temperatures cannot be represented by the first order kinetics (Figure 10). An initial rapid decline was followed by an exponential decay in conductivity suggesting existence of

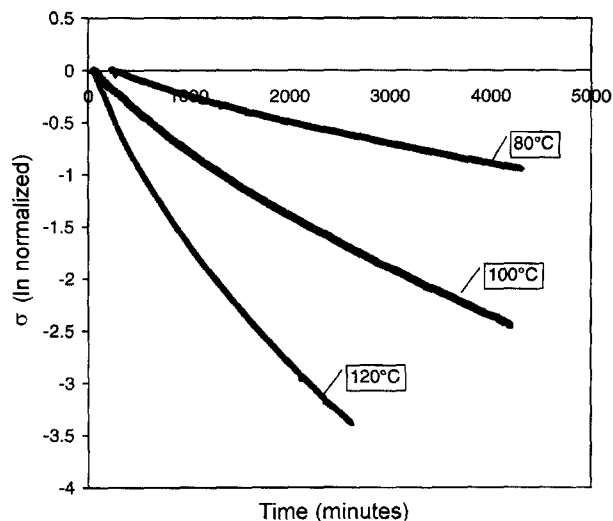


Figure 10. Natural logarithm of normalized conductivity vs. time (minutes) of lightly doped Ppy/pTS (0.005 mol/lit).

two different degradation mechanisms.

Microwave Transmission

When microwaves impinge on a material, reflection, transmission and absorption of the radiation take place in varying degrees depending on the frequency of the radiation and electrical properties of the material. Electromagnetic shielding effectiveness (SE) is the attenuation of an electromagnetic wave during its passage through a conductor and is expressed in dB.

The skin depth is defined as the surface thickness of a conducting material at any frequency for which 1-1/e or 63.2 percent of the current is flowing through. That is for 99% of the current flow, 4.6 skin depths are required. Often the thickness *t* of the shield is considered to be satisfactory when, *t* > δ. Skin depth is inversely proportional to the frequency of the impinging radiation and conductivity of the material and is expressed as:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{1}$$

where, *f*: frequency of the impinging radiation (Hz)
 μ: permeability of the free space (4π × 10⁻⁷ H/m)
 σ: electrical conductivity of the shield (S/m).

For example at 10 GHz the skin depth for copper and highly doped PPy film with a conductivity of 40 S/cm are 0.66 and 79.6 microns respectively.

A comprehensive review[15] and studies on electromagnetic shielding effectiveness and various microwave properties of intrinsically conducting polypyrrole films and polymer composites have been reported[12,16-23]. In this study the effect of aging time and dopant anion concentration on the

insertion loss (IL) (transmission coefficient), return loss (RL) (reflection coefficient) and shielding effectiveness (SE) of the polypyrrole films at microwave frequencies were investigated. Reflection coefficient is a log ratio of the amplitude of reflected field strength to the amplitude of the incident field strength. Transmission coefficient is the log ratio of the amplitude of the transmitted field strength to the incident field strength and both are expressed in decibels. SE can be defined as the summation of IL and RL values in decibels.

As seen in Figure 11, highly doped films are very reflective. The highly doped (0.05-M/lit pTS) film exhibits high SE values that are quite stable with a decrease of about 20% in dB within an aging period of one-year. The corresponding

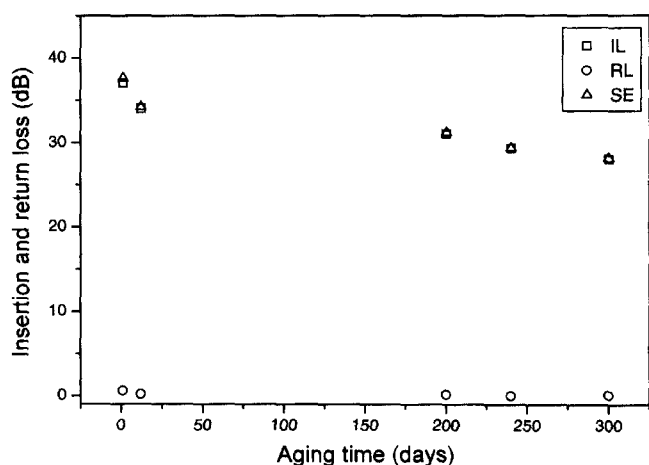


Figure 11. Influence of aging on insertion loss, return loss and shielding effectiveness of 0.05 M/lit pTS doped polypyrrole films at 10 GHz.

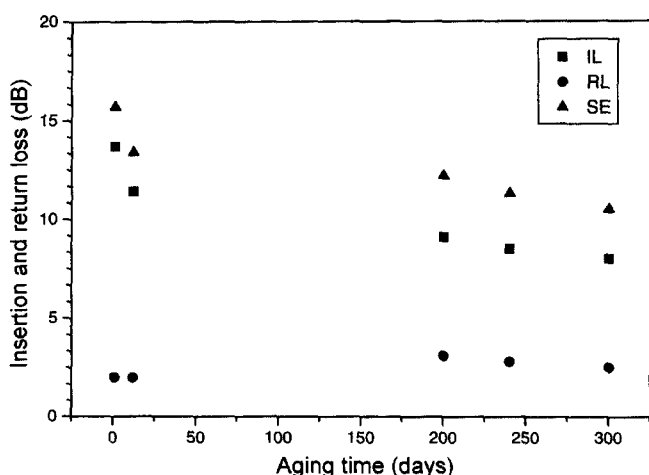


Figure 12. Influence of aging on insertion loss, return loss and shielding effectiveness of 0.005 M/lit pTS doped polypyrrole films at 10 GHz.

return loss values are extremely low. The lightly doped (0.005-M/lit) film, on the other hand, is less stable. It loses about 40% of its SE in dB within one year and has lower IL and higher RL values compared to that of 0.05-M/lit film (Figure 12). The difference in the microwave-aging behavior of highly and lightly doped films can clearly be seen in Figure 13 when the results are expressed in percent transmission. Highly doped film clearly shows a very stable transmission profile, indicating a high retention of reflectivity. On the other hand, lightly doped films are less stable with a significant increase in microwave transmission during the aging period. For example, the reduction of insertion loss from 37 dB to 30 dB within a period of one year corresponds to an increase in percent transmission through the highly doped film from 0.02% to 0.1%. The conductivity of this film decreased from 35 S/cm to 27 S/cm within this period.

The decrease in the insertion loss of the lightly doped film from 13.7 dB to 8 dB within one year corresponds to an increase in transmission from 7.2% to 15.85%. Due to their lower electrical conductivity, lightly doped films were partially reflecting, transmitting and hence absorbed a significant portion of the incident radiation (Figure 13). For example, the freshly synthesized lightly doped PPy film transmitted 13.7%, reflected 64% and absorbed 22.3% of the incident radiation. These results show that slight loss of conductivity in highly doped films does not affect their shielding ability significantly within the period of aging whereas the shielding ability of lightly doped was affected significantly within the aging period. These results are in agreement with those obtained from degradation of conductivity, which showed distinct differences in the aging behavior of highly and lightly doped films.

The differences in the initial microwave transmission of highly and lightly doped films can also be explained by referring to equation (1) for the skin depth. For example, the

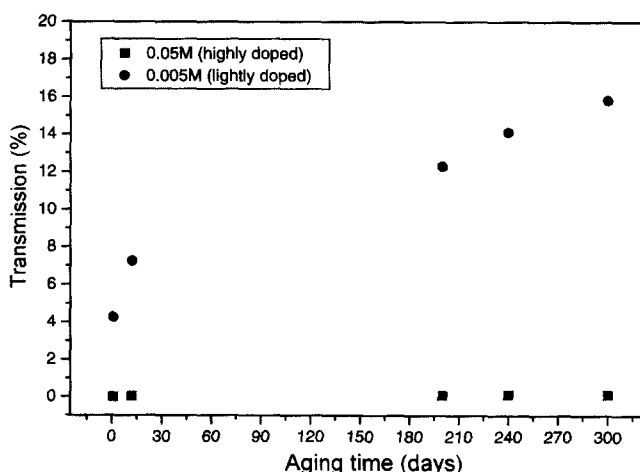


Figure 13. Influence of aging on percent transmission of highly and lightly doped films at a frequency of 10 GHz.

skin depth at 10 GHz for a highly doped film with an electrical conductivity of 34 S/cm is 86.3 microns. As the film thickness is comparable to skin depth it is reasonable to obtain such low transmission values. On the other hand, in the case of a lightly doped PPy film the skin depth is considerably larger than the film thickness, in agreement with the high transmission results obtained in the experiments.

Infrared Spectroscopy

Some spectral observations on the effects of room temperature aging on lightly doped PPy films have already been reported in an earlier publication[24]. FT-IR spectra from 2000 cm^{-1} to 800 cm^{-1} of a lightly doped polypyrrole film at progressive stages of room temperature aging have been studied. The loss of conductivity of polypyrrole films with aging in air was attributed to the reaction between polymer backbone and oxygen, forming α , β -unsaturated carbonyl groups. It was suggested that carbonyl groups constituted a trapping site in the conduction process by causing disruptions in the conjugation[24]. Further FTIR spectroscopic studies on highly and lightly doped films confirmed the growth of carbonyl group with aging time (Figure 14). However, there was no sign of carbonyl growth

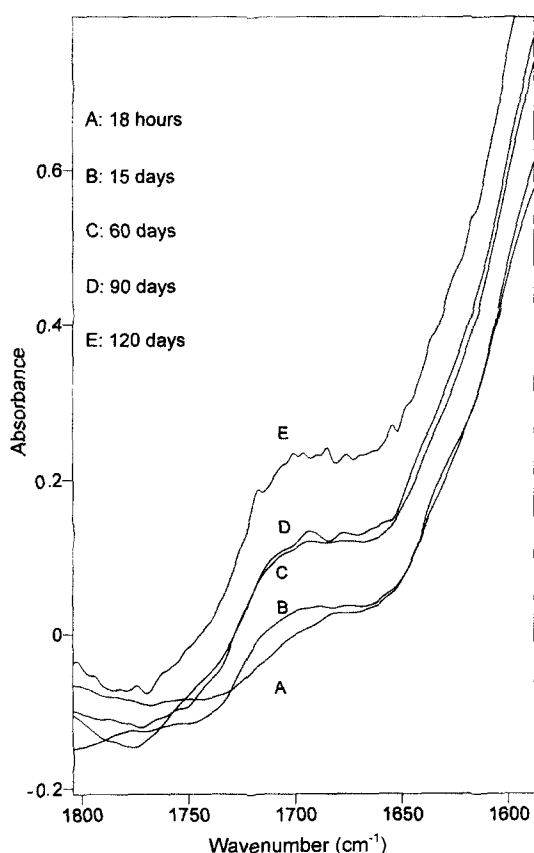


Figure 14. Change in carbonyl intensity with aging time of lightly doped polypyrrole.

in the spectra of highly doped PPy films, even after 10 months of aging. This observation also reinforced the statement that degradation trend is influenced by the concentration of the dopant anion and highly pTS doped PPy is more stable than lightly doped PPy.

Acknowledgements

The author would like to thank Dr. Thor Borston from the Analytical Electron Microscopy Facility, Queensland University of Technology for his help in electron microscopy. Thanks to Dr. Llew Rintoul from the Centre for Instrumental and Developmental Chemistry at Queensland University of Technology for his help in FTIR spectroscopy. The author also wishes to express special thanks to Professor Graeme George, Dean of Faculty of Science at Queensland University of Technology for his interest and valuable discussions.

References

1. A. Kaynak, *Mat. Res. Bull.*, **32**, 271 (1997).
2. K. J. Wynne and G. B. Street, *Macromolecules*, **18**, 2361 (1985).
3. M. Ogasawara, K. Funahashi, and K. Iwata, *Mol. Cryst. Liq. Cryst.*, **118**, 159 (1985).
4. R. C. D. Peres, J. M. Pernaut, and M.-A. De Paoli, *J. Polym. Sci., Part A, Polym. Chem.*, **29**, 225 (1991).
5. B. F. Cvetko, M. P. Brungs, R. P. Burford, M. Skyllas, and Kazacos, *J. Mater. Sci.*, **23**, 2102 (1988).
6. M. Gandhi, G. M. Spinks, R. P. Burford, and G. G. Wallace, *Polymer*, **36**, 4761 (1995).
7. L. J. Buckley, D. K. Roylance, and G. E. Wnek, *J. Polym. Sci., Part B, Polym. Phys.*, **25**, 2179 (1987).
8. Bloor, R. D. Hercliff, C. G. Galiotis, and F. J. Young in "Electronic Properties of Polymers and Related Compounds", H. Kuzmany (M. Mehring and S. Roth Eds.), p. 179, Springer Verlag, Berlin, 1979.
9. J. Unsworth, P. C. Innis, B. A. Lunn, Z. Jin, and G. P. Gordon, *Synth. Met.*, **53**, 59 (1992).
10. G. R. Mitchell, F. J. Davis, and M. S. Kiani, *Polymer*, **23**, 157 (1990).
11. A. Kaynak, *Mat. Res. Bull.*, **33**, 81 (1998).
12. J. Unsworth, A. Kaynak, B. A. Lunn, and G. E. Beard, *J. Mat. Sci.*, **28**, 3307 (1993).
13. L. A. Samuelson and M. A. Druy, *Macromolecules*, **19**, 824 (1986).
14. X. B. Chen, J. Devaux, J.-P. Issi, and D. Billaud, *Eur. Polym. J.*, **30**, 809 (1994).
15. J. Rodriguez, H. J. Grande, and T. F. Otero, "Handbook of Organic Conductive Molecules and Polymers: Vol. 2. Conductive Polymers: Synthesis and Electrical Properties", (H. S. Nalwa Ed.), Chap. 10, p.413, John Wiley and Sons, New York, 1997.
16. A. Kaynak, J. Unsworth, and G. Beard, R. Clout, *Mat. Res.*

- Bull.*, **28**, 1109 (1993).
17. A. Kaynak, *Mat Res. Bull.*, **31**, 845 (1996).
18. A. Kaynak, J. Unsworth, A. Mohan, and G. E. Beard, *J. Appl. Polym. Sci.*, **54**, 269 (1994).
19. A. Kaynak, A. Polat, and U. Yilmazer, *Mat Res. Bull.*, **31**, 1195 (1996).
20. M. W. Rupich, Y. P. Liu, and A. B. Kon, *Mater. Res. Soc. Symp. Proc.*, **293**, 163 (1993).
21. N. F. Colaneri and L. W. Shacklette, *IEEE Trans. Instrum. Meas.*, **41**, 291 (1992).
22. J. Joo and A. J. Epstein, *Appl. Phys. Lett.*, **65**, 2278 (1994).
23. P. Kathirgamanathan, *Adv. Mater.*, **5**, 281 (1993).
24. A. Kaynak, L. Rintoul, and G. A. George, *Mat Res. Bull.*, **35**, 813 (2000).