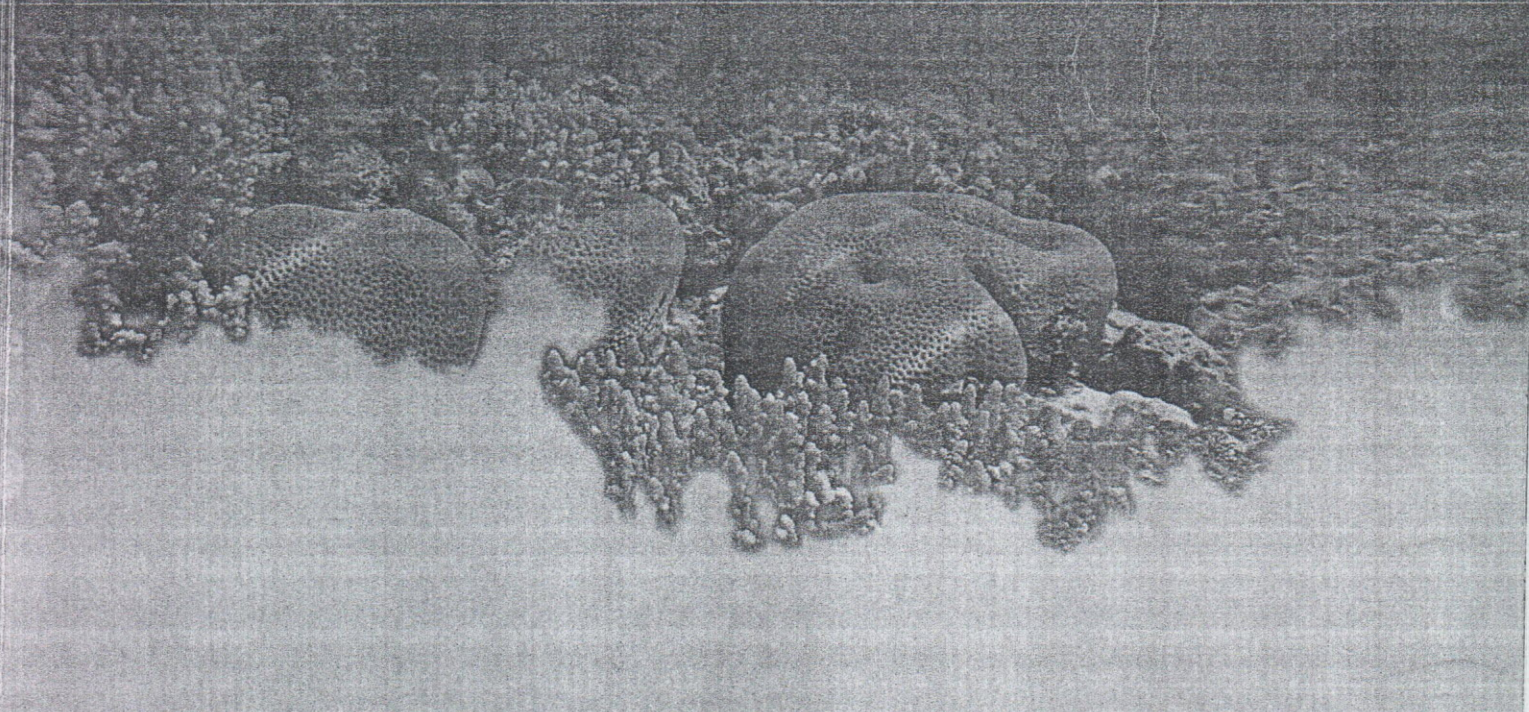


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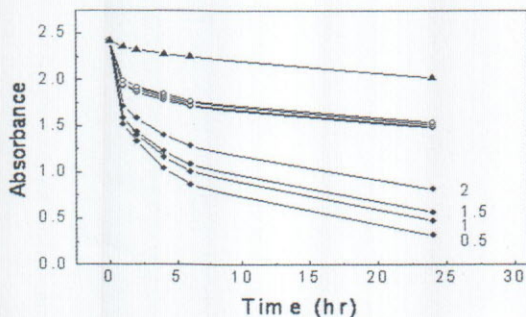
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Book of Abstracts

to prepare the most efficient DPPH free radical scavenger for PANI, PPy and PEDOT were 1.5, 0.5 and 1, respectively. After reaction with DPPH for 24 hrs, around 70% of the DPPH free radicals were quenched by PANI and PPy, but only 16 % by PEDOT. This represents a 3 to 1 ratio of pyrrole units to DPPH•, 2 to1 for aniline units and 9 to1 for EDOT units. To further examine the electron transfer process in the DPPH assay, reduced forms of PANI and PPy were evaluated. The reduction of PANI and PPy with hydrazine led to a complete loss of (bi)sulfate dopant, but to improved DPPH radical scavenging, confirming that the conducting polymer is acting as a reducing agent in scavenging DPPH radicals. The antioxidant activity of PPy and PANI films prepared by an electrochemical method were evaluated using a further standard food science antioxidant assay, the oxygen radical absorption capacity (ORAC) assay.[5] The results showed that both PPy and PANI show peroxy free radical scavenging activity, and that these two conducting polymers are excellent free radical scavengers. The polymers can be contrasted to the small molecule antioxidants generally found in foods and beverages with prospects for extension of shelf-life in packaging applications.



INVESTIGATING THE KINETICS POLYMERIZATION OF POLY(O-METHYLANILINE) [PTu16]

The polymerization kinetics of poly(o-methylaniline) prepared from the chemical oxidation of o-methylaniline with ammonium peroxydisulfate at several monomer:oxidant concentration ratio in 1 molL⁻¹ hydrochloric acid medium was investigated. The reaction was investigated by UV-Vis spectroscopy and the rate constants were calculated. The absorption spectra shows a decrease in the band at 350nm attributed to oxidant, and another an enhancement in the band at 650nm, attributed to polymer. The absorption of the band in 350nm was linearized with $-dA/dt=kA$ equation. The value of experimental constant rate was determined as $(8.8 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$. A equation was proposed to study the band in 656nm. The values of experimental constants rate was determined as $k_i = 4.5 \times 10^{-3} \text{ s}^{-1}$, $k_g = 2.6 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_t = 6.6 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_2' = 186 \text{ L mol}^{-1} \text{ s}^{-1}$. The effect of LiCl addition on the reaction rate was investigated resulting a increase in the rate constants by increasing the ionic strength. It was observed that the reactant species in solution are charged and have the same electrical charge.

[1] M. Gizdavic-Nikolaidis, J. Travas-Sejdic, G.A. Bowmaker, R.P. Cooney and P.A. Kilmartin, *Synth. Met.* 140 (2004) 225. [2] P.A. Kilmartin, M. Gizdavic-Nikolaidis, Z. Zujovic, J. Travas-Sejdic, G.A. Bowmaker, R.P. Cooney, *Synth. Met.* 153 (2005) 153. [3] H. Wang, L.H. Zhu, J. Li, H.Q. Tang, *Chin. Chem. Lett.* 18 (2007) 1005. [4] C.F. Hsu, L. Zhang, H. Peng, J. Travas-Sejdic and P.A. Kilmartin, *Curr. Appl. Phys.* 8 (2008) 316. [5] B.X. Ou, M. Hampsch-Woodhill, R.L. Prior, *J. Agric. Food Chem.* 49 (2001) 4619. Figure 1: 516 nm absorbance for 255 μM DPPH in methanol after the addition of 1 mg of (○) PEDOT, (●) PPy, or for (▲) DPPH only. The ratio of APS to pyrrole used to form the polymers is also indicated. Acknowledgement The authors gratefully acknowledge the New Zealand Foundation for Research, Science and Technology for financial support (NERF UOAX0408).



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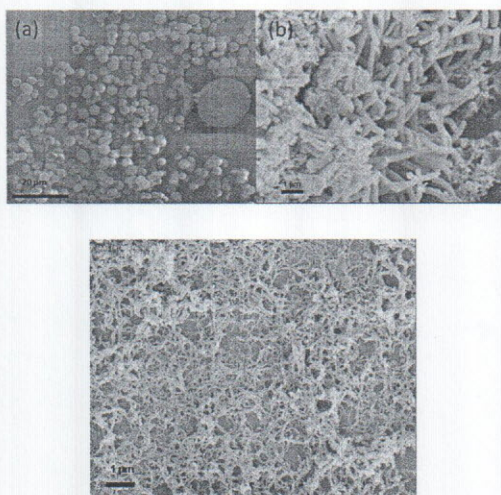
OXIDATIVE CHEMICAL SYNTHESIS OF POLYMERIC NANO/MICRO STRUCTURES FROM MONOMERIC ANILINES [PM12]

In view of the increasing activity in nano-science and nano-technology, it is of interest to reexamine and build upon earlier observations of organic polymers, which were of much of interest in the past primarily because of their unusual electronic properties [1]. The sensitivity of the type of nano/micro morphology on the synthetic method employed including variation in pH, temperature, and absolute reactant concentration, opens up a vast unexplored potential field, which has not as yet been tapped. For example, chemical and/or electrochemical synthesis of an electroactive polymer, such as polyaniline, alone yields a wide variety of materials depending on the pH of the system [2] and morphologies ranging from the first reported synthesis of nanofibers of polyaniline [3] to the dependency of the nucleation step and resulting morphology on the nature of the counter ion [4], to the chemical synthesis of polypyrrole which can yield a matte-like film or nanospheres [5]. In the past, much excellent research has been carried out world-wide on "polyaniline"—its chemical and electrochemical synthesis, characterization and electronic, magnetic, optical, and related properties [6]. Polyaniline and its derivatives have attained considerable world-wide importance principally because of their unique set of electronic properties. In this work, our results show that the nature of the product obtained by the oxi-



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oxidative polymerization of aniline depends critically on the synthesis condition used, such as: initial pH of the reaction system and the absolute concentration of the reagents. Specifically, we found that the solid product isolated (Figure 1(a,b) - (a) Hollow microspheres, average diameter: 1.5–6 μm . (b) Nanotubes, average inner tube diameter: 40 nm) from the aqueous polymerization system containing aniline, hydrochloric acid, and ammonium peroxydisulfate with a higher pH can be completely different in chemical composition, spectroscopic properties, and morphology from the "polyaniline" obtained using the same reagents at the usual lower pH value of ~ 0 (Figure 2 – Nanofibers, average fiber diameter: 44 nm) [3,6]. The aqueous oxidative polymerization of aniline in a sufficiently low pH is divided into two hypothetical parts [2] — Part A: polymerization; Part B: protonation by the H_2SO_4 produced or by any other acid that has been added to the polymerization system. It should be noted that the quantity of acid formed during the polymerization step significantly exceeds the amount of acid required in the protonation step—hence, a net increase in acid concentration during polymerization is observed, and it is, in part, responsible for the generation of a large variety of nano/micro morphology obtained from the oxidative aqueous polymerization of aniline.



A NANOCARRIER CHARGE MODEL FOR THE TRANSPORT IN POLY(O-ALKOXYANILINES) [PTu19]

The mechanisms for charge transport and the nature of the charge species have been controversial. Here we propose a structural model for poly(o-alkoxyanilines), where the conduction process is governed by nanocarriers or quasi-particles with concomitant hopping and tunneling between conducting islands. The metallic islands are coupled into the network with the twisted and tangled polymer chains. We studied the formation of charge carriers in poly(o-alkoxyanilines) using electron paramagnetic resonance (EPR), which shows the presence of two types of charge carriers in poly(o-alkoxyaniline) solutions for an intermediate pH value ($\text{pH}=5.0$). The first type is localized in the amorphous part and with small mobility, while the second is delocalized in the semi-crystalline part with high mobility. Using small-angle X-ray scattering (SAXS) we confirm the existence of quasi-particles in solution, corroborated by ab initio procedures based on simulated annealing (see Fig. 1). The model also indicates that the quasi-particles may jump between defects along the polymer chain providing electronic conduction, which are consistent with molecular modeling results (ab initio and semi-empirical). However, it does not discard the hopping process between neighboring chains.



Figure 1. Average Dummy Atom Model (DAM) in pH 3.0 (HCl).

[1] T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, Handbook of Conducting Polymers, second ed., Marcel Dekker, New York, 1998. [2] E.C. Venancio, P.-C. Wang, A.G. MacDiarmid, Synth. Met. 156 (2006) 357. [3] W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 1 82 (1986) 2385. [4] A.J. Motheo, J.R. Santos Jr., E.C. Venancio, L.H.C. Mattoso, Polymer 39 (1998) 6977. [5] P.-C. Wang, R.E. Lakis, A.G. MacDiarmid, Thin Solid Films 516 (2008) 2341. [6] A.G. MacDiarmid, Angew. Chem. Int. Ed. 40 (2001) 2581. Acknowledgements: CNPq, Fapesp, CAPES, FINEP and University of Pennsylvania.



Fabio de Lima Leite (USP/Embrapa (Brazil)), Marcelo Luiz Simões (Embrapa (Brazil)), Mário de Oliveira Neto (USP (Brazil)), Ranylson Marcello Leal Savedra (USP (Brazil)), Paulo Sérgio de Paula Herrmann Junior (Embrapa (Brazil)), Igor Polikarpov (USP (Brazil)), Ladislau Martin Neto (Embrapa (Brazil)), Milan Trsic (USP (Brazil)), Luiz Henrique Capparelli Mattoso (Embrapa (Brazil)), Osvaldo Novais de Oliveira Junior (USP (Brazil))