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Effect of Humidity on AC Conductivity of Polyaniline and Poly(O-Methoxyaniline)

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Polianilina e poli(o-metoxianilina) foram sintetizadas quimicamente com persulfato de amônia e preparados na forma de filmes flexíveis e auto-sustentáveis por solução de N-metil pirrolidona. As propriedades elétricas destes filmes foram investigadas por medidas de impedância na faixa de freqüência de 10^{-2} a 10^{5} Hz, sob vácuo e 70% de umidade relativa.

A componente real da condutividade e a tangente delta foram calculadas. A condutividade é constante na região de baixa freqüência e aumenta a altas freqüências. A baixas freqüências a condutividade aumenta significativamente com o aumento da umidade. Este efeito é mais acentuado para a poli(o-metoxianilina) devido à presença do grupo polar. Os resultados de condutividade AC podem ser ajustados usando mecanismos de "hopping" por um modelo associado a distribuição de taxas de transição.

Polyaniline and poly(o-methoxyaniline) were chemically synthesized with ammonium peroxydisulfate and casted as flexible free-standing films using N-methyl pyrrolidone. The electrical properties of these films were investigated using impedance measurements within a frequency range of 10^{-2} to 10^{5} Hz, under vacuum and in air at 70% relative humidity.

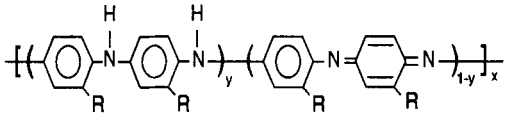
The real component of the conductivity, as well as the tangent δ data were obtained. The conductivity is constant in the low frequency range and increases significantly in the high frequency range. The low frequency conductivity is higher when the polymer is in a humid atmosphere, especially in the case of poly(o-methoxyaniline) due to the presence of a polar group. The experimental results can be fitted by hopping using a distribution of transition rate method.

Keywords: *conducting polymers, polyanilines, electrical properties*

Introduction

Conducting polymers have been widely studied due to their extremely interesting and unusual electrical, electrochemical and optical properties, which have made possible a large range of technological applications. Recently, due to an electrical behavior similar to metals, these properties have come to include the processability, mechanical strength and chemical stability of conventional polymers[1].

Polyaniline and its derivatives play a important role in the conducting polymer field due to their low cost, ease of doping and extremely good stability in the doped state[2]. Also, these polymers are soluble in common organic solvents, making possible the casting of flexible, free-standing films[3]. Polyanilines have the general base composition given below:



where y denotes the polymer oxidation state and R = H for parent polyaniline. For instance, when y = 0.5 the polymer is in the half-oxidized state, namely emeraldine, which, after doping by protonation, leads to the most conductive form of polyanilines[4]. Several polyaniline derivatives can

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be synthesized e.g. poly(o-methoxyaniline), when group R is replaced by OCH_3.

In this work, we report the effect of humidity on impedance studies of parent polyaniline and poly(o-methoxyaniline) films in the frequency range of 10^{-2} to 10^5 Hz. A quantitative model is applied for the wide range of conductivity dependence.

Experimental

Polymer synthesis

Parent polyaniline - PANI and poly(o-methoxyaniline) - POMA were chemically synthesized with ammonium peroxydisulfate as the oxidant in 1.0 M HCl at 0 °C, using a previously described method[5]. The monomer to oxidant ratio used was 4:1. Since classical chemical synthesis produces low molecular weight POMA (Mw ~ 30,000 g/mol) whose mechanical strength is not enough to cast flexible films, we have used a novel method[6] developed to produce high molecular weight POMA (Mw ~110,000 g/mol). The polymerization was terminated after about 3 h by filtering and washing with 1.0 M HCl and acetone for PANI and POMA, respectively. The polymers in the powder form were then deprotonated with ammonium hydroxide for 16 h and dried under dynamic vacuum for 24 h.

Film preparation

The polymers synthesized and deprotonated as described above were obtained in the de-doped emeraldine base oxidation state, which is more soluble in organic solvents than the HCl-doped polymers. Solutions containing 2% polymer in N-methyl pyrrolidone were prepared, cast in glass slides, and placed in an oven at 55 °C for 16 h to evaporate the solvent. Flexible, free-standing films were obtained after detaching the polymer from the glass by immersion in water. It was important to leave the films to dry between two paper filters and glass slides under pressure to ensure film planarity.

Measurements

Rectangular samples of the polymers (2.5 cm x 3.5 cm, 12 μm thick) were used, each with a rectangular (2 cm^2) gold deposit (900 Å thick) on both sides as an electrode. Impedance measurements were performed using a Potentiostat/Galvanostat (EG&G/PARC Model 273A) coupled with a Frequency Response Analyzer (Solatron Model HF 1255) and controlled by a EG&G/PARC software Model 388 in the frequency range of 10^{-2} to 10^5 Hz. The experiments were performed under vacuum or in ambient humidity, at room temperature.

Results and Discussion

The experimental data obtained for POMA in air at 70% relative humidity are shown in Fig. 1 in a Nyquist plot. To convert these experimental impedance data into the complex admittance, the following equation was used:

$$Y^* = (Z^*)^{-1} = Y' + jY'' \quad (1)$$

where Y^* is the complex admittance, Z^* is the complex impedance, Y' and Y'' are, respectively, the real and imaginary admittance, and $j = \sqrt{-1}$.

Hodge *et al.*[11] have proposed equation 2 for calculating conductivity within the range of frequency of the experiments:

$$Y^* = (Z^*)^{-1} = j\,\omega\,C_o\,\varepsilon^* \quad (2)$$

where C_o is the vacuum capacitance, ω is the angular frequency, and ε^* is the complex permittivity.

Figure 2 shows the results of real conductivity measurements of PANI and POMA base as a function of frequency performed under vacuum. The conductivity remains constant up to about 10^2 Hz where it begins to increase with increasing frequency, obeying the relation $\sigma(\omega) \propto \omega^s$ with $s \cong 1$. PANI presents higher conductivity than POMA in the whole range of frequency investigated (10^{-2} to 10^5 Hz), but at high frequencies they tend towards the same value. A similar behavior is observed when the experiment is carried out in an environment with 70% relative humidity, as shown in Fig. 3. However, in the presence of moisture the conductivity of POMA is higher than that of PANI, contrary to that observed under vacuum. In a previous work[3] it was shown that the conductivity of parent polyaniline increases with the absorption of water by the sample. Indeed, this is the case for both polyanilines studied, with the effect being more prominent for the o-methoxy substituted polyaniline, where an increase of 2.5 x 10^{-11} to

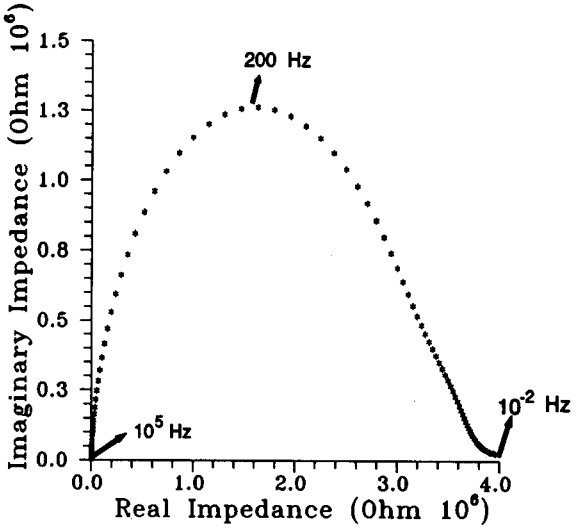

Figure 1. Nyquist plot for poly(o-methoxyaniline) (POMA) in 70% relative humidity, in the frequency range of 10^{-2} to 10^5 Hz.

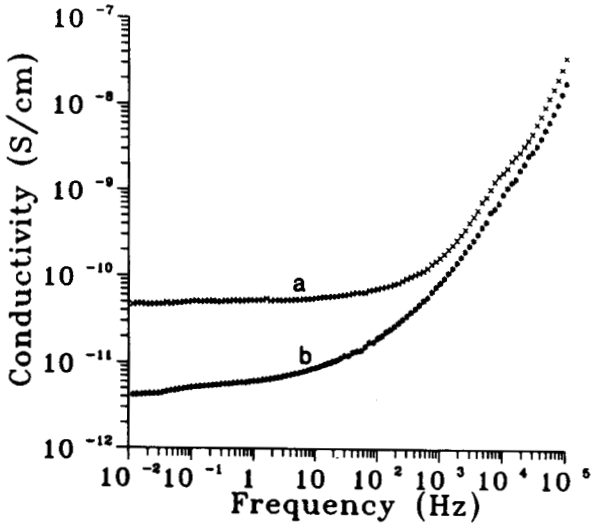

Figure 2. Real electrical conductivity as a function of frequency for a) PANI base, and b) POMA base. Measurements performed under a 10^{-3} Torr vacuum.

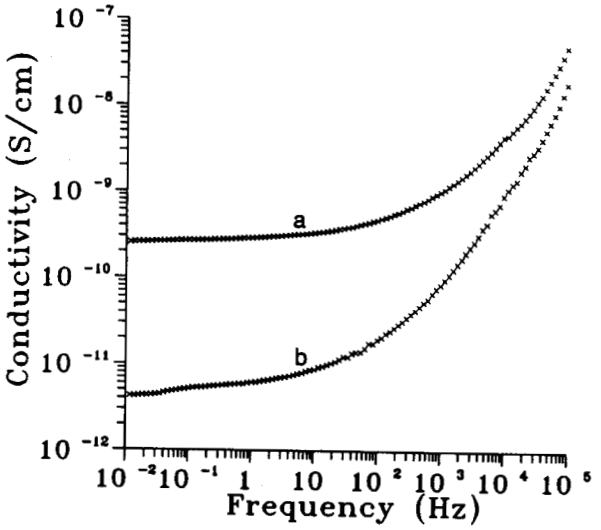

Figure 4. Real electrical conductivity of POMA base as a function of frequency, performed under: a) 70% relative humidity, and b) 10^{-3} Torr vacuum.

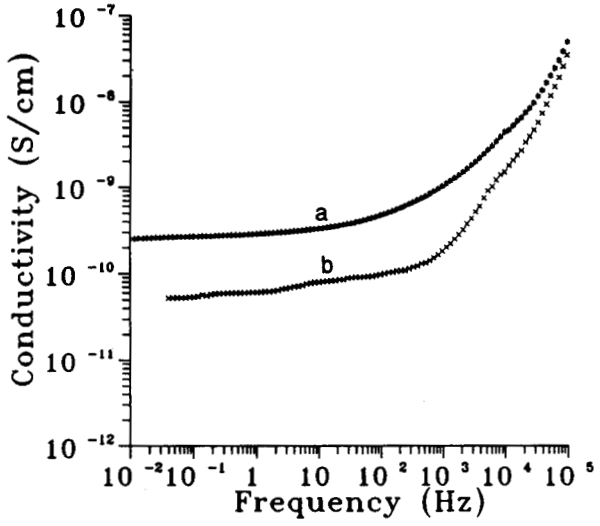

Figure 3. Real electrical conductivity as a function of frequency for a) POMA base, and b) PANI base. Measurements performed under 70% relative humidity.

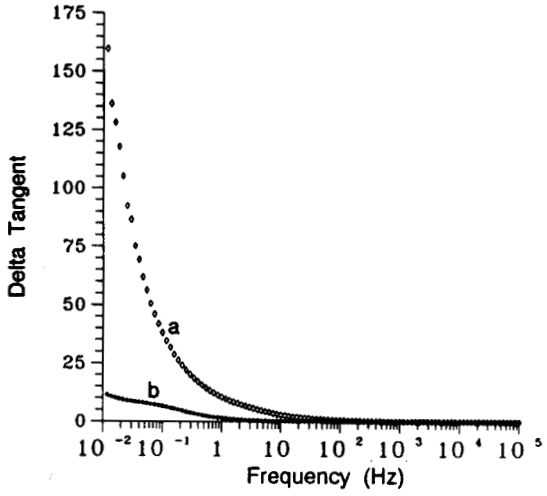

Figure 5. Delta tangent as a function of frequency for POMA performed under: a) 70% relative humidity, and b) 10^{-3} Torr vacuum.

1.5×10^{-9} S/cm is observed (Fig. 4). This might be due to the higher hydrofilicity of the polar substituent of POMA. Similarly, the tangent delta (Fig. 5) at low frequencies is much higher in 70% relative humidity than in vacuum, but is about the same in the high frequency range.

Several models have been proposed for continuous and alternated conductivity in disordered materials in the last decades. One of them is the pair approximation model[7] based on the transition between localized state pairs, which has provided the explanation for many experimental results for several materials. However, this model is limited to the high frequency range[8].

Other models such as the continuous time random walk (CTRW) model[9] and the effective medium (EM) model[10] have demonstrated good agreement in a wide range of frequencies, from high (~10^7 Hz) to low (~10^{-3} Hz). Experimental results from glassy and semiconducting materials indicate a constant conductivity for low frequency up to a critical frequency (ω_c), where it starts to increase with ω^s, (for $s < 1$). For much higher frequencies (above GHz) the conductivity becomes constant again. The experimental results for POMA and PANI, under vacuum and in a humid environment (Figs. 2 to 5), show similar behavior, with a constant conductivity for low frequencies and obeying the

relation $\sigma(\omega) \cong \omega^s$ above 10^3 Hz. A theoretical model was used to describe the dependence of the conductivity as a function of frequency. This model is equivalent to CTRW, where an average of the distribution of the transition rate is made[9]. We use the transition rate distribution (P(V)) proposed by Pareto[12] which has explained, with great accuracy, the conductivity of a wide range of semiconductors. This distribuition is given by

$$P(V) = \frac{(1-S)\,V^{-s}}{V_{max}^{1-s} - V_{min}^{1-s}} \quad (3)$$

where V_s is the fundamental transition rate, s is the slope of log σ *vs.* log ω plots when $\omega >> \omega_c$, and V_{max} and V_{min} are, respectively, the lower and the upper cutoffs in the spectrum of transition rates.

Equation 3 can be originated from hopping distance distribution, from trap depth distribution, or from activation energy distribution[14]. The values of P(V) were calculated using an average for the conductive system equivalent to a series in transition rate[12].

The fit of the model with the experimental data from POMA is shown in Fig. 6. One can observe an excellent description of the dependence from 10^{-2} to 1 Hz and from 10^3 to 10^4 Hz. A small deviation is observed in the other frequency ranges which are much smaller than that observed using other models for fitting[12,13]. Specifically, the Pareto[12] distribution for the transition rate was used, which limits the highest and lowest values cutting the transition rate spectrum.

Conclusions

The conductivity of PANI and POMA, considered potential conductive polymers, have presented behavior similar to that observed in semiconductors and glassy inorganic materials within a wide frequency range. It was also observed that moisture increases the conductivity of these materials, especially in the case of POMA, without any modification in the shape of the curve $\sigma(\omega)$. The behavior of $\sigma(\omega)$ is well explained by hopping mechanisms used for disordered materials, using a distribution of transition rates P(V), specifically the Pareto distribution.

Acknowledgments

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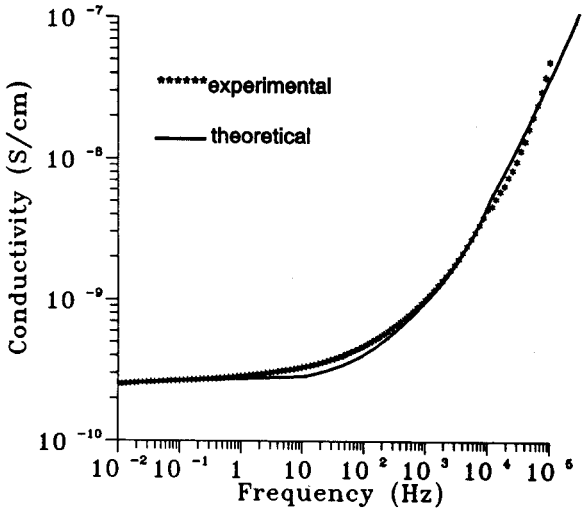

Figure 6. Fitting of the real component of AC conductivity as a function of the frequency in 70% relative humidity.

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