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Microwave transmission, reflection and dielectric properties of conducting and semiconducting polypyrrole films and powders

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Microwave transmission, reflection and some dielectric properties of the conducting polymer, polypyrrole, are presented. Methods are discussed for determining microwave transmission and reflection of electrochemically synthesized and doped polypyrrole films with conductivities ranging from 0.1–5000 $\mathrm{S\,m^{-1}}$. Polypyrrole films were placed between waveguides and irradiated with microwaves centred at frequencies 2.45 and 10 GHz with 0.1 GHz span. The results indicate that the conductivity of doped polypyrrole films has a significant effect on both transmission and reflection. Microwave opacity of polypyrrole varied with the synthesis conditions of the polymer. Samples with low conductivity exhibited high transmission whereas low transmission readings were observed with highly conducting films. Dielectric properties are also presented for frequencies from 100 to 10^6 Hz in a temperature range of 90–280 K and at microwave frequencies of 2.45 and 10 GHz. These measurements indicate that the real and imaginary parts of the dielectric constant increase in magnitude with increasing doping level.

1. Introduction

The mechanical, electrical and dielectric properties of electrochemically synthesized conducting polymers are influenced by their synthesis parameters. Conducting polymers can be synthesized by electrochemical and chemical methods and they can be made to possess a wide range of electrical conductivities by varying the anion doping level. For example, polypyrrole shows good mechanical and electrical stability and is synthesized electrochemically with conductivities ranging from 0.1–5000 $\mathrm{S\,m^{-1}}$ [1]. Other synthesis parameters such as pH and temperature also influence the morphological properties of polypyrrole [2].

There has been little investigation of the dielectric properties of polypyrrole at microwave frequencies. Analysis of the frequency dependence of the electrical conductivity of conducting polymers has led to different research groups being critical of certain representations of the results [3, 4]. This criticism has arisen due to the presence of two schools of thought [5] in presenting the frequency-dependent electronic properties of materials, i.e. using either a dielectric or a conductivity representation. In this paper, both representations are employed where appropriate.

Study of alternating-current (a.c.) conduction at microwave frequencies for several types of polypyrrole [6] has been undertaken with the dopant type and concentration influencing the resultant properties.

The dielectric properties of highly doped polypyrrole films were investigated [7] with the real and imaginary parts of the complex dielectric constant decreasing in magnitude with increasing frequency.

The conductivity and dielectric constant of emeraldine polymer has been studied at 6.5 GHz as a function of temperature and protonation levels with a range of electrical conductivities from insulating to conducting [8]. The microwave conductivity has been found to be much larger than direct-current (d.c.) conductivity for the insulating base, but microwave conductivity approaches the d.c. conductivity for higher conductivity emeraldine salts. The dielectric constant has been found to increase linearly with protonation for emeraldine salts while the temperature dependence of microwave conductivity differs from the d.c. conductivity dependence, particularly at low temperatures.

In this paper the transmission coefficient, reflection coefficient and complex dielectric constant for polypyrrole films and powders with a range of doping levels are determined at frequencies of 2.45 and 10 GHz.

2. Experimental techniques

2.1. Conducting-polymer synthesis

A galvanostatic electrochemical synthesis method was employed for the oxidative polymerization of polypyrrole [1]. The main advantage of the galvanostatic technique is that, as it is a bulk-electrolysis technique, large-surface-area films can be synthesized. A two-electrode cell was employed, with polymerization occurring at a horizontally oriented stainless-steel-type-304 anode. Stainless-steel gauze suspended above the anode was employed as the cathode. A pyrrole concentration of 0.2 M in aqueous solution was used. Polypyrrole films of varying electrical conductivities were synthesized using a range of p-toluenesulphonate (p-TS) anion dopant concentrations. The variation of conductivity of the film synthesized with the concentration of dopant [p-TS] can be seen in Fig. 1. During the preparation of the supporting electrolyte, and prior to pyrrole addition, the pH of the solution was adjusted to approximately 11 to completely deprotonate the p-TS into the anion form. Synthesis was carried out at an optimum current density of 3.0 A cm^{-2} over 30 min at 2 °C to yield a film of the order of 50 μm in thickness. The conductivity of the resulting film was determined using the standard four-probe method.

Free-standing films were peeled from the anode using a scalpel and vacuum dried. If not tested immediately, the films were stored at − 10 °C in the dark. Powders for use in the cavity perturbation method were produced using a microhammer mill.

2.2. Microwave measurements and analysis techniques

Microwave experiments were undertaken using a Hewlett–Packard Network Analyser 8720A. Initially, polypyrrole film was sandwiched between Teflon cylinders and inserted into a coaxial transmission line which was designed to operate in the frequency range of 2.0–12.0 GHz. However difficulties were encountered in placing the polypyrrole film reproducibly inside the coaxial transmission line.

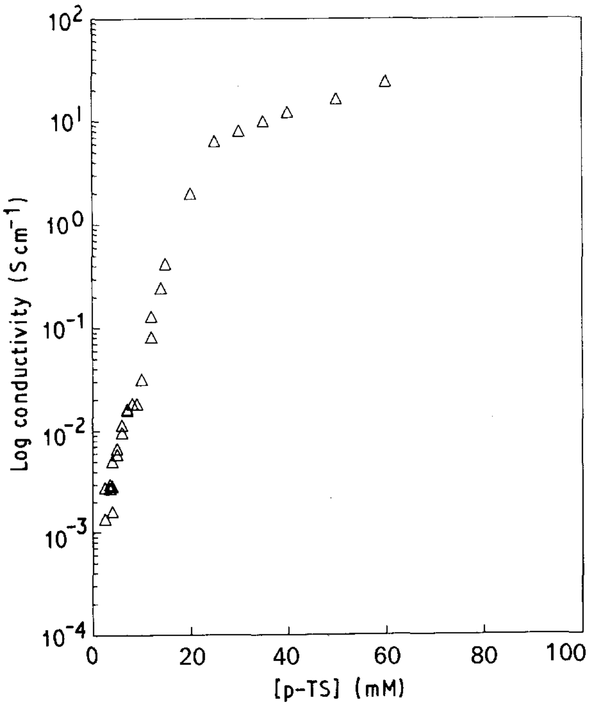

Figure 1 Electrical conductivity versus dopant concentration of polypyrrole films.

The experiments were improved by sandwiching the samples between two waveguide-to-coaxial transducers and carrying out the analysis at frequencies of 2.45 and 10 GHz with a span of 0.1 GHz. High precision coaxial cables were used and the analyser was calibrated before each use on the face of the transducers using appropriate coaxial standards, together with a suitable electrical delay. Reflection and transmission coefficients for the polymer film were obtained by clamping free-standing films of polypyrrole between the waveguide transducers and then irradiating them with microwaves.

For complex-dielectric-constant measurements of polypyrrole powders at microwave frequencies, a conventional cavity perturbation technique at a resonant frequency of 2.45 GHz was used. The cavity perturbation technique, being a contactless complex-dielectric-constant-measurement method, avoided resistance and capacitance contributions to measurements. Swept frequencies were employed using the analyser connected to a TM_{012} cylindrical resonant cavity of fixed dimensions. The changes in Q-factor and the resonant frequency of the cavity with and without the sample in the cavity were measured. Inserting the sample in the cavity gave rise to a shift of the cavity resonant frequency to a lower value and reduction of the cavity quality factor. Standard perturbation equations for a cylindrical TM_{012} cavity to evaluate complex dielectric constants [9, 10] have been used. For this method, polypyrrole powder was pressed into a disc-shaped Teflon sample holder, located in the centre of the cavity to produce the maximum effect since the electric field is a maximum along the central axis.

The method of cavity perturbation is based on a small perturbation, which means that the specimen-to-cavity-radius ratio, R_s/R_c (R in metres), should be in the region of one twentieth or less. The fractional shift of frequency and quality factor are given by Equations 1 and 2, respectively [9].

$$\mathrm{d}f/f_0 = (\varepsilon' - 1)ABG(V_s/V_c) \qquad (1)$$

where df is the shift in frequency (Hz), ε' is the permittivity of the sample, V_s is the sample volume (m^3) and V_c is cavity volume (m^3)

$$(1/Q_s - 1/Q_c) = 2\varepsilon'' ABG(V_s/V_c) \qquad (2)$$

where Q_s, Q_c are the quality factors of the loaded and unloaded cavity, ε'' is the sample loss and A, B, C, G are defined by

$$A = J_0^2(2.405R_s/R_c) + J_1^2(2.405R_s/R_c) \qquad (3)$$

$$B = 1 + \frac{L_c}{2\pi L_s}\sin\frac{2\pi L_s}{L_c}\cos\frac{4\pi H}{L_c} \qquad (4)$$

$$G = 0.2718\left(\frac{v_0}{f_0 + R_c}\right)^2 \qquad (5)$$

and

$$df = f_0 - f_s \tag{6}$$

where, H is the height of the sample above the bottom of the cavity (m), L_s is the length of the sample (m), L_c is the cavity length (m), f_0 is the resonant frequency of the unloaded cavity (Hz), f_s is the resonant frequency of the loaded cavity (Hz), and $J_0(x)$ and $J_1(x)$ are zeroth and first-order Bessel functions of the first kind. For nondestructive and more precise evaluations of complex dielectric constants a resonant-window method designed for testing sheet materials was employed [11]. The polypyrrole film was placed in a resonant window situated midway along a rectangular transmission-type cavity operating in the TE_{103} mode. Two resonant-window rectangular cavity sets operating at 10 and 2.45 GHz were designed and fabricated by using the following equation [11]

$$\frac{a}{b}\left[1-\left(\frac{\lambda_0}{2a}\right)^2\right]^{1/2} = \frac{t}{h}\left[1-\left(\frac{\lambda_0}{2t}\right)^2\right]^{1/2} \tag{7}$$

where λ_0 is the free-space wavelength, and a, b are the outer and t, h the inner dimensions of the resonant window.

The real and imaginary parts of the complex dielectric constant were calculated from the following equations

$$\varepsilon' = 1 + \frac{\ell(f_L - f_0)}{zgf_L} \tag{8}$$

and

$$\varepsilon'' = \frac{\ell(Q_0 - Q_L)}{2zgQ_LQ_0} \tag{9}$$

where, ℓ is the length of the rectangular cavity (m), f_0 is the unloaded resonant frequency (Hz), f_L is the loaded resonant frequency (Hz), Q_0 is the unloaded quality factor, Q_L is the loaded quality factor, z is the sample thickness (m), g is the geometric factor of the resonant window. Before testing polypyrrole, samples with known dielectric constants at microwave frequencies, such as various types of wood and plastics, were tested using both techniques and the results were found to agree with published data [12].

3. Results and discussion

3.1. Transmission and reflection

In electromagnetic theory a good conductor is a medium for which $\sigma/\omega\varepsilon \ll 1$. With the exception of a few samples with low conductivity, around $10^{-1}\,\mathrm{S\,m^{-1}}$, tested at 10 GHz, polypyrrole samples satisfied the good conductor condition. Therefore, microwave transmission and reflection could be examined using standard concepts in electromagnetic theory, such as skin depth, δ.

Initial experiments showed that microwave transmission and reflection varied with the synthesis conditions of the polymer [10]. Further analysis of the microwave energy after transmission through and reflection from the polypyrrole at 10 GHz are plotted with respect to z/δ in Fig. 2, where z is the sample thickness in metres. Microwave energy was plotted as a function of the polymer's skin depth, δ, in order to examine the influence of conductivity (i.e. doping level) whilst removing the effect of variations in thickness since skin depth, δ, is given by

$$\delta = (2/2\pi f\sigma\mu)^{1/2} \tag{10}$$

where, σ is the sample conductivity ($\mathrm{S\,m^{-1}}$), μ is the permeability of free space ($\mathrm{Fm^{-1}}$) f is the frequency of incident microwave radiation (Hz).

Reflection, transmission and absorption of microwave radiation at 10 and 2.45 GHz, as a function of polypyrrole doping level are shown in Figs 3 and 4. The corresponding electrical conductivity can be determined by referring to Fig. 1. At very low electrical conductivities of polypyrrole, in the order of $10^{-1}\,\mathrm{S\,m^{-1}}$, transmission of microwave radiation through the film is very high with very little reflection.

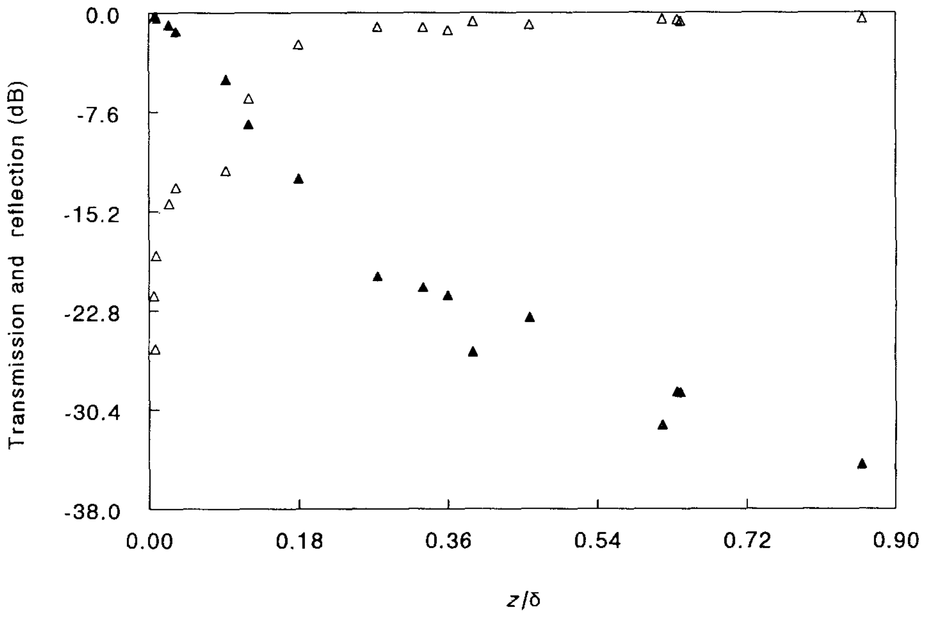

Figure 2 Microwave reflection and transmission versus z/δ of polypyrrole films at 10 GHz: (△) reflection, and (▲) transmission.

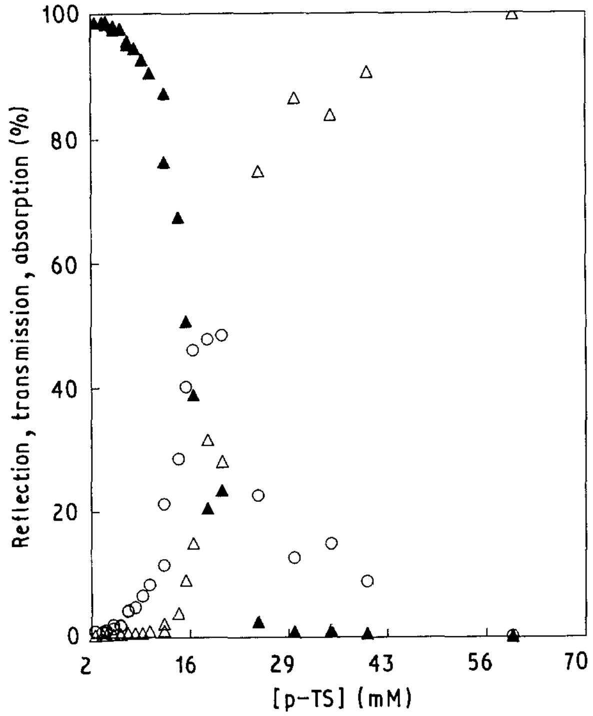

Figure 3 Microwave reflection, transmission and absorption versus the dopant concentration of polypyrrole films at 10 GHz: (△) reflection, (▲) transmission, (○) absorption.

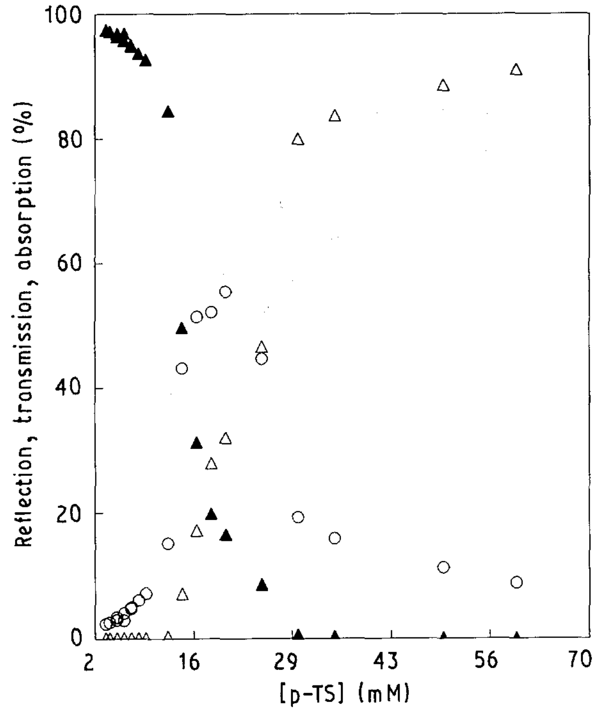

Figure 4 Microwave reflection, transmission and absorption versus dopant concentration of polypyrrole films at 2.45 GHz: (△) reflection, (▲) transmission, (○) absorption.

At such low doping levels there is very little interaction of the microwaves with the material. Conversely, at high electrical conductivities 1–5 × 10^3 S m^{-1}, microwave reflection is very high with almost no transmission. At high doping levels, polypyrrole behaves like a metal with the collapse of the electric-field component of the microwave radiation occurring when it impinges on the high-conductivity film. However, at intermediate doping levels, where there is maximum rate of change in reflection and transmission, a maximum in microwave absorption was observed at both 10 and 2.45 GHz. This peak in absorption suggests that the microwave radiation causes excitation of charge carriers at relatively low doping levels.

3.2. Dielectric results

The variation of the real and imaginary parts of the complex dielectric constant with sample conductivity can be seen in Figs 5, 6 and 7. Both ε' and ε'' increased with increasing dopant concentration. A similar trend of increasing ε' was observed in conducting emeraldine salts [8] with increasing protonation for intermediate-level and high-level protonated emeraldine salts and for epoxy-aluminium particle composites [13] when aluminium concentration increased.

Using the imaginary part of the complex dielectric constant, ε'' values, obtained by the cavity perturbation method in the microwave region and substituting into the following equation (from [14])

$$\omega\varepsilon_0\varepsilon'' = \sigma_m(\omega) - \sigma_{dc} \tag{11}$$

where, $\omega = 2\pi f$, ε'' is the imaginary part of the dielectric constant, σ_{dc} is the d.c. conductivity of the polymer film obtained by the standard four-probe technique, $\sigma_m(\omega)$ is the microwave conductivity.

The microwave conductivities of lightly doped polypyrrole films at 10 GHz are detailed in Table I.

The electrical conductivity evaluated at 10 GHz was higher than the d.c. conductivity measured for the lightly doped samples.

Equation 11 is only applicable to lightly doped films as the presence of a significant d.c. conductivity masks any dielectric response. This correlates with frequency-dependent conductivity results taken at lower frequencies (100–10^6 Hz) using a Hewlett–Packard 4194A Impedance Gain–Phase Analyser. At these fre-

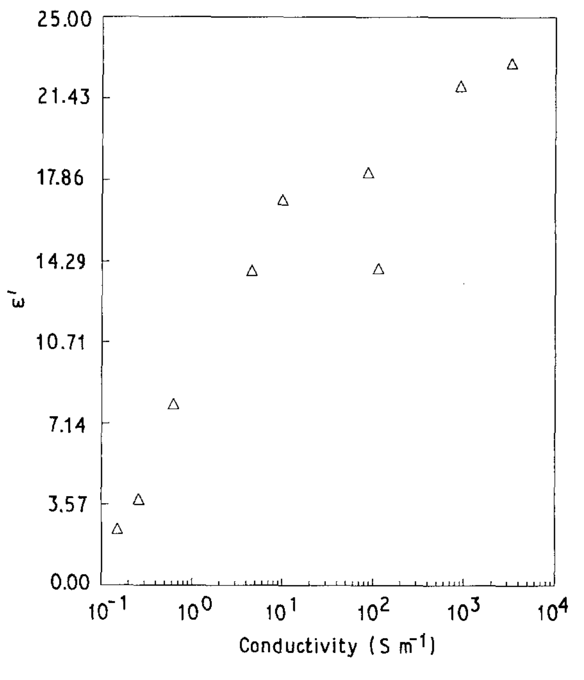

Figure 5 ε' versus electrical conductivity at 2.45 GHz by cylindrical cavity perturbation.

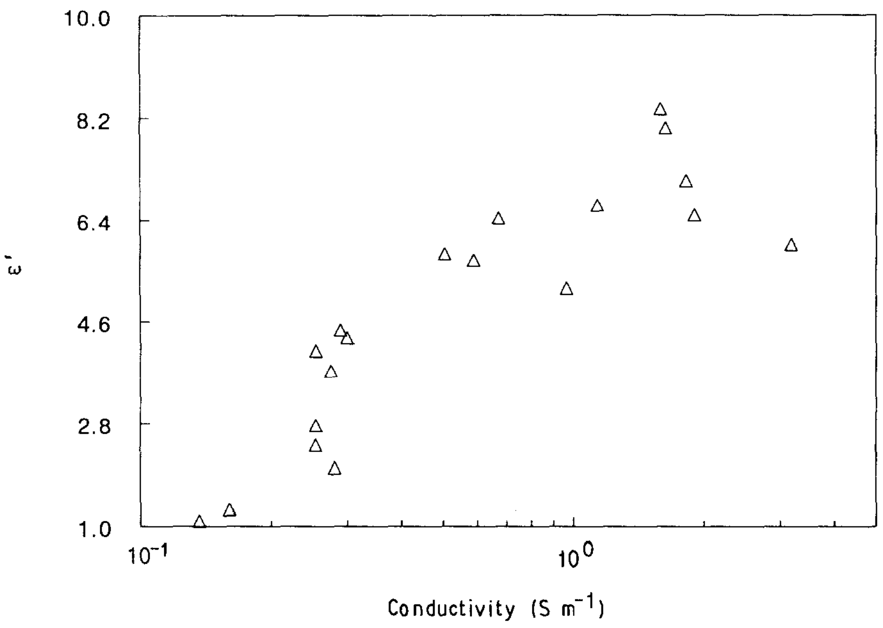

Figure 6 ε′ versus electrical conductivity at 10 GHz by the resonant-window method.

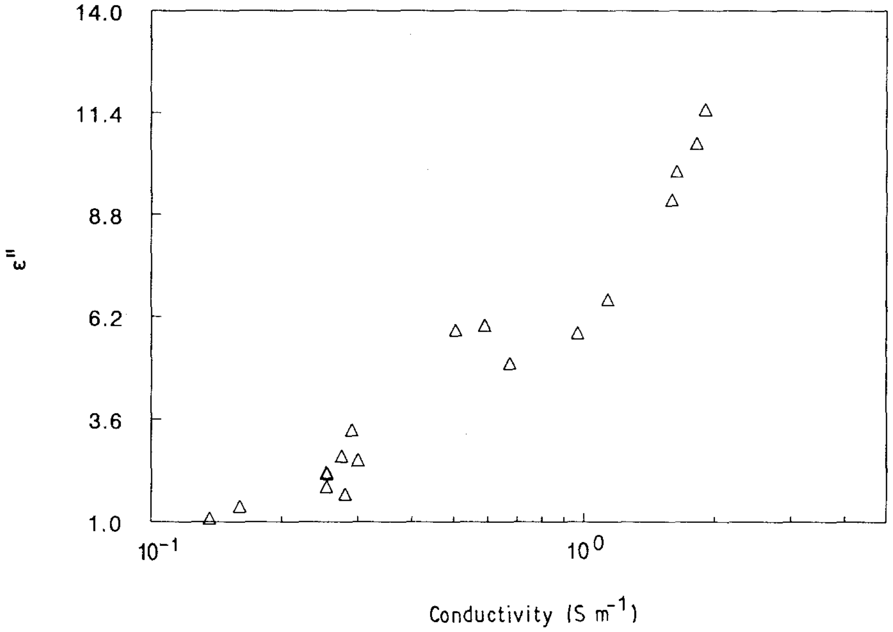

Figure 7 ε″ versus electrical conductivity at 10 GHz by the resonant-window method.

TABLE I Dielectric and conductivity properties of lightly doped polypyrrole films

σ_{dc} (S m^{-1})	ε′	ε″	tan δ	$\sigma(\omega)_m$ (S m^{-1})	[Dopant] (M)
0.28	2.031	1.717	0.845	0.943	0.0025
0.25	2.431	1.9	0.781	1.043	0.0025
0.25	2.775	2.264	0.816	1.243	0.0025
0.30	4.322	2.578	0.597	1.414	0.0035
0.29	4.454	3.34	0.75	1.832	0.004
0.503	5.805	5.863	1.01	3.215	0.004
0.588	5.692	5.983	1.051	3.28	0.005
0.762	6.446	5.027	0.78	2.753	0.005
1.135	6.68	6.644	0.995	3.64	0.005
0.965	5.196	5.8	1.116	3.178	0.006
1.635	8.035	9.918	1.234	5.423	0.007
1.59	8.365	9.179	1.097	5.02	0.007
1.9	6.507	11.491	1.766	6.287	0.008
1.82	7.107	10.627	1.495	5.81	0.009

quencies an a.c. component of electrical conductivity was not observable in highly conducting polypyrrole films over the temperature range 90–290K (Fig. 8). While for semiconducting polypyrrole films, an a.c. component of conductivity was measurable at all temperatures (Fig. 9).

The use of Equation 11 for disordered materials, such as polypyrrole, is subject to conjecture, however, since both the d.c. and a.c. components may be interrelated and then the d.c. component cannot be simply subtracted from the total measured conductivity [3].

In contrast with the results presented in this paper, dielectric constants of polypyrrole doped with p-TS anion – from reflection and transmission data using Fresnel equations – gave values of approximately 10^4 in the microwave regime [7]. This difference suggests that the measurement technique employed affects the dielectric constant determined.

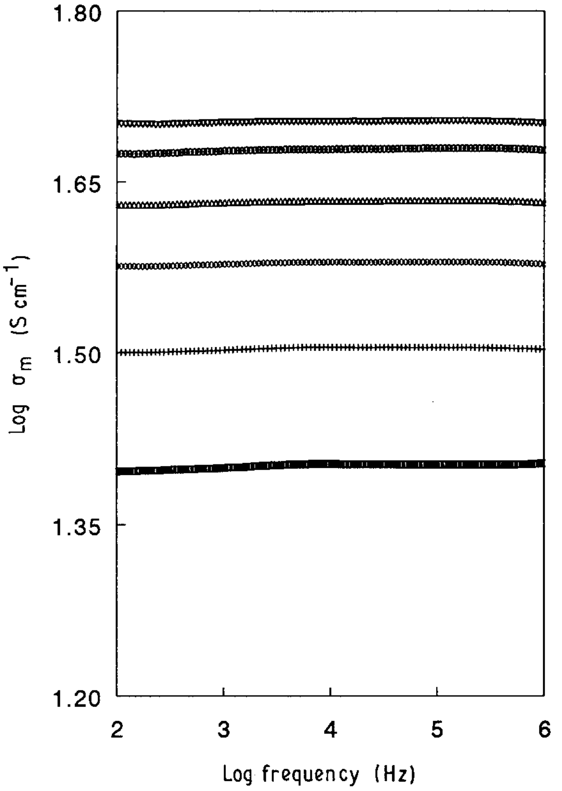

Figure 8 Measured conductivity as a function of frequency and temperature for conducting polypyrrole film. (□) 90 K, (+) 130 K, (◇) 170 K, (△) 210 K, (○) 251 K, and (▽) 290 K.

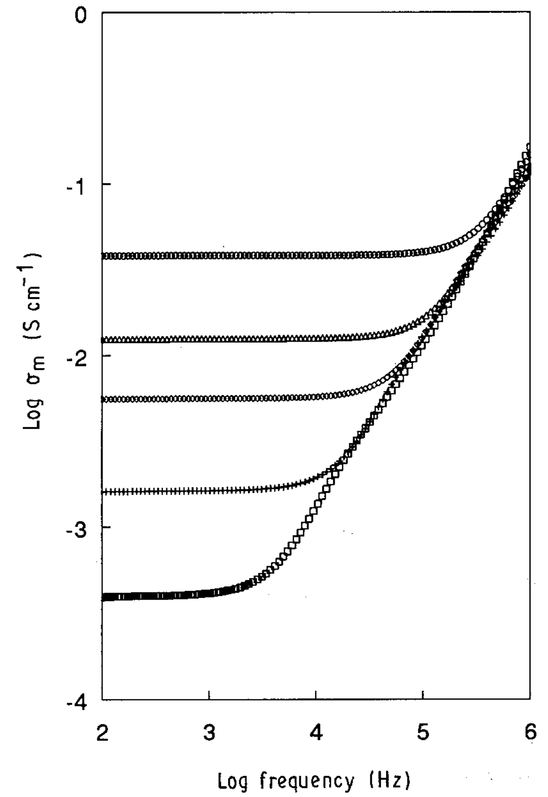

Figure 9 Measured conductivity as a function of frequency and temperature for semiconducting polypyrrole film: (□) 136 K, (+) 170 K, (◇) 210 K, (△) 250 K, and (○) 290 K.

4. Conclusion

Polypyrrole films display a wide range of electrical properties that can be obtained by relatively simple electrochemical and chemical processes. The polymer can easily be synthesized to produce predetermined values of reflection, transmission, absorption, conductivity and permittivity in the microwave regime.

The sensitivity of the microwave properties of the polymer to the doping level during synthesis combined with the stability of its electrical and mechanical properties may lead to novel microwave applications and devices.

Further experiments on dielectric properties of the polymer are currently being made over a wide temperature range to elucidate the microwave properties and therefore gain insight into structure and conduction mechanisms with a view to potential applications.

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