Study of Dielectric Properties of Polypyrrole Prepared using Two Different Oxidizing Agents

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ABSTRACT: Polypyrrole samples that have been prepared in a conducting state by a chemical method using two different oxidizing agents, ferric chloride and potassium persulphate, in different concentrations have been transformed to a dielectric state by heating at 333 K for 7 days and then at 353 K for 4 days more. Then the frequency and temperature 32 dependence of the dielectric constant ε', loss tangent tan δ and AC conductivity σ' were investigated using a complex impedance technique. It has been found that the concentrations of the reactants used in the preparation have a noticeable effect on the dielectric properties. It has been concluded also that heating at constant temperature has enhanced the resistivity of the samples, which can be considered as a simple method of obtaining polypyrrole (PPy) in a dielectric state rather than more complex electrochemical methods which may be useful in some future applications such as the manufacture of supercapacitors. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3370–3379, 2006

INTRODUCTION

The enormous interest demonstrated in the last few years for the research in conductive polymers is mainly due to the large number of potential technological applications for these materials.[1] In spite of the significant research efforts in this area, the actual conduction mechanism in these materials still require elucidation.[2] In conducting the polypyrrole, the most likely assumed mechanism is that the polymer backbone structure is conjugated (alternating single and double bonds) and the existence of an ionic dopant in the polymer results in a delocalization of the double bond electrons giving "near" metallic conductivity.[3] Studying the dielectric properties (dielectric function, AC conductivity, and loss tangent) of a material may be useful in applications in the field of capacitor manufacture, besides it may lead to a better clarification of conduction or charge transport mechanism, therefore the aim of the present work is to study the dielectric properties of polypyrrole (PPy) after transforming it from its conducting state to a dielectric state by prolonged heating.

EXPERIMENTAL

Polypyrrole samples have been prepared in a conducting state by a chemical method using two different oxidizing agents, ferric chloride and potassium per-

sulphate, in different concentrations. The resistance of the samples was measured by using a Keithley 617 Programmable electrometer, where it was found to have values less than 2 kΩ for all samples. The samples have been transformed to a dielectric state by heating at 333 K for 7 days then at 353 K for 4 days more. The resistance had been checked again with the electrometer and was found to be in the range of 200 kΩ–1 MΩ. The real part of the dielectric function (the dielectric constant) ε', the dielectric loss factor tan δ, and the real part of the AC conductivity function σ' were measured using the complex impedance technique (lock-in amplifier, Stanford Research Systems Model SR830 DSP). The details of the used circuit were previously published elsewhere.[4]

RESULTS AND DISCUSSION

Frequency dependence of the dielectric constant ε'

Figures 1(a)–1(g) show the frequency dependence of the dielectric constant ε' at different temperatures for the studied samples. It can be observed that ε' decreases as the frequency f increases at all values of temperature. This behavior of the dielectric constant is similar to that of the reported for other polymers.[5, 6] The high values of ε' at low frequencies are due to interfacial polarization i.e., the building up of bound charges at interfaces within the bulk samples. This interfacial polarization occurs in heterogeneous structures due to the accumulation of charges at the interfaces between various regions that differ from each other in its DC conductivity.[7]

In polymers, the interfacial polarization is caused by the dispersion of islands of conductive regions in the
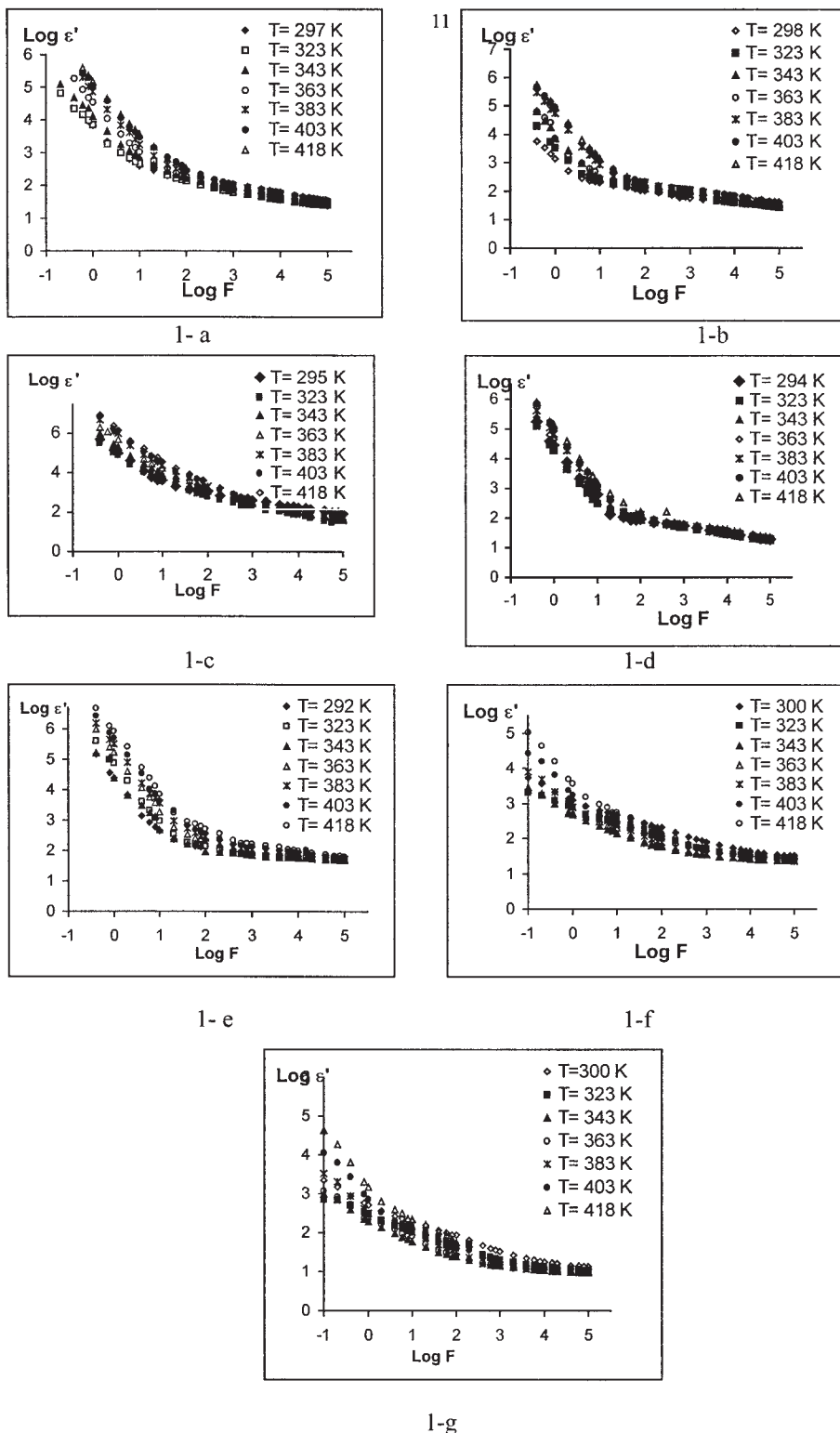
Figure 1 The frequency dependence of the dielectric constant ε' at different temperatures and at different concentrations of ferric chloride (PY : FeCl$_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : K$_2$S$_2$O$_8$ = 1 : 2 (e), 1 : 2.5 (f), 1 : 3 (g)).

polymer within an insulating matrix as previously stated by Rocha et al.[8] Moreover, there is also accumulation of bound charges at the interfaces between the sample and the electrodes that adds to the net polarization (electrode polarization). This space charge accumulation introduces an extra capacitive

component into the system.[9] Moreover, it is known that at low frequencies, when the temperature increases, the side groups or small units of main chains may be able to move and follow the variation of the field and therefore may contribute to the polarization, while on increasing frequencies, those side groups or small units of main chains lose gradually their ability to follow the field and consequently their contribution to the polarization ceases.[7]

Temperature dependence of the dielectric constant ε'

Figures 2(a)–2(g) show the temperature dependence of the dielectric constant ε' at some selected frequencies. It is seen that, at low frequencies, the dielectric constant increases significantly with increasing temperature, this behavior shows the thermally activated nature of charge transport in the samples resembling semiconductor. At high frequencies, there is a less noticeable increase in ε' with increase in temperature and this can be related to the disability of charges to follow the fast variations in the applied field as the frequency increases.

Frequency dependence of the real part of the ac conductivity σ'

Figures 3(a)–3(g) show the frequency dependence of the real part of the AC conductivity σ' at different temperatures. At frequencies of the range 10^3–10^5 Hz, there is an obvious increase in the real part of AC conductivity σ' with increasing frequency and the samples seem to obey a well known universal law of the form $\sigma'(\omega) = \sigma_{dc}(T) + A(T)\,\omega^s$,[6, 10] where $A(T)$ is a constant depending on the temperature and s is the frequency exponent and its value has been always found between 0 and 1.[11] At lower frequencies of the range 10^3–1 Hz, in all samples, we can observe that $\sigma'(f)$ becomes almost independent of frequency. This may be due to random diffusion of the charge carriers via activated hopping, which is known to give rise to a frequency independent conductivity.[12] At very low frequencies ($\leq$1 Hz) there may be a contribution—due to the electrode polarization—to σ', which increases with increasing frequency.

Temperature dependence of σ'

Figures 4(a)–4(g) show the temperature dependence of σ' at some selected frequencies where we can see that at low temperatures, the AC conductivity shows a stronger dependence of frequency, where the dielectric relaxation is dominant.[13] At higher temperatures, the AC conductivity (σ') increases—as previously mentioned—while its dependence on frequency decreases. It is also noticeable in Figure 4(e) that the

sample of the ratio (Py:$K_2S_2O_8$ = 1:1.5) shows an obvious frequency independence of the conductivity, which makes this sample a good candidate for manufacturing of resistors.

Frequency dependence of the dielectric loss factor tan δ

Figures 5(a)–5(g) show the frequency dependence of the dielectric loss factor tan δ at different temperatures. It is shown that, tan δ increases as the frequency increases, reaching a maximum value or a peak and then decreases as the frequency further increases. Some of those peaks shift to higher frequencies as the temperature increases. It is known that, in most physical interpretations of relaxation processes in polymers, a peak has been assigned to a particular mode of motion in the main chain, a side chain, or a side group in the polymer matrix.[14] In the present case it is believed that transport processes is mainly performed by activated hopping of π-electrons so that the peaks of tan δ are suggested to occur when the most probable relaxation time of the hopping electrons coincides with the applied frequency.

Frequency dependence of the electric modulus M^*

In many instances, the dynamics of interest are seemed to be better understood by plotting data in one of several alternatives, which are equivalent representations.[15] Although data representation in M^* (the electric modulus which is equal to $1/\varepsilon^*$) is physically equivalent to data representation in ε^* formalism, in some cases the M^* representation becomes useful since space charge effects can be suppressed and the conductivity current relaxation is best studied.[6] Figures 6(a)–6(g) show the frequency dependence of the real part of the electric modulus M' at different temperatures. It can be seen that M' exhibits a part of a sigmoid shape and the values of M' increase with increasing frequency as reported by other authors in other polymers.[12] Figures 7(a)–7(g) show the frequency dependence of the imaginary part of the electric modulus M'' at different temperatures, where M'' also exhibits peaks. Those peaks are known to be observed in the region of the onset of AC conductivity. Moreover, those peaks shift to higher frequencies with increasing temperature, implying higher energies of the current charge carriers at higher temperatures, since it is known that peaks in $M''(f)$ plots are caused by conductivity current relaxation.[6]

The effect of reactants' concentrations on the dielectric constant, ac conductivity, and tan δ

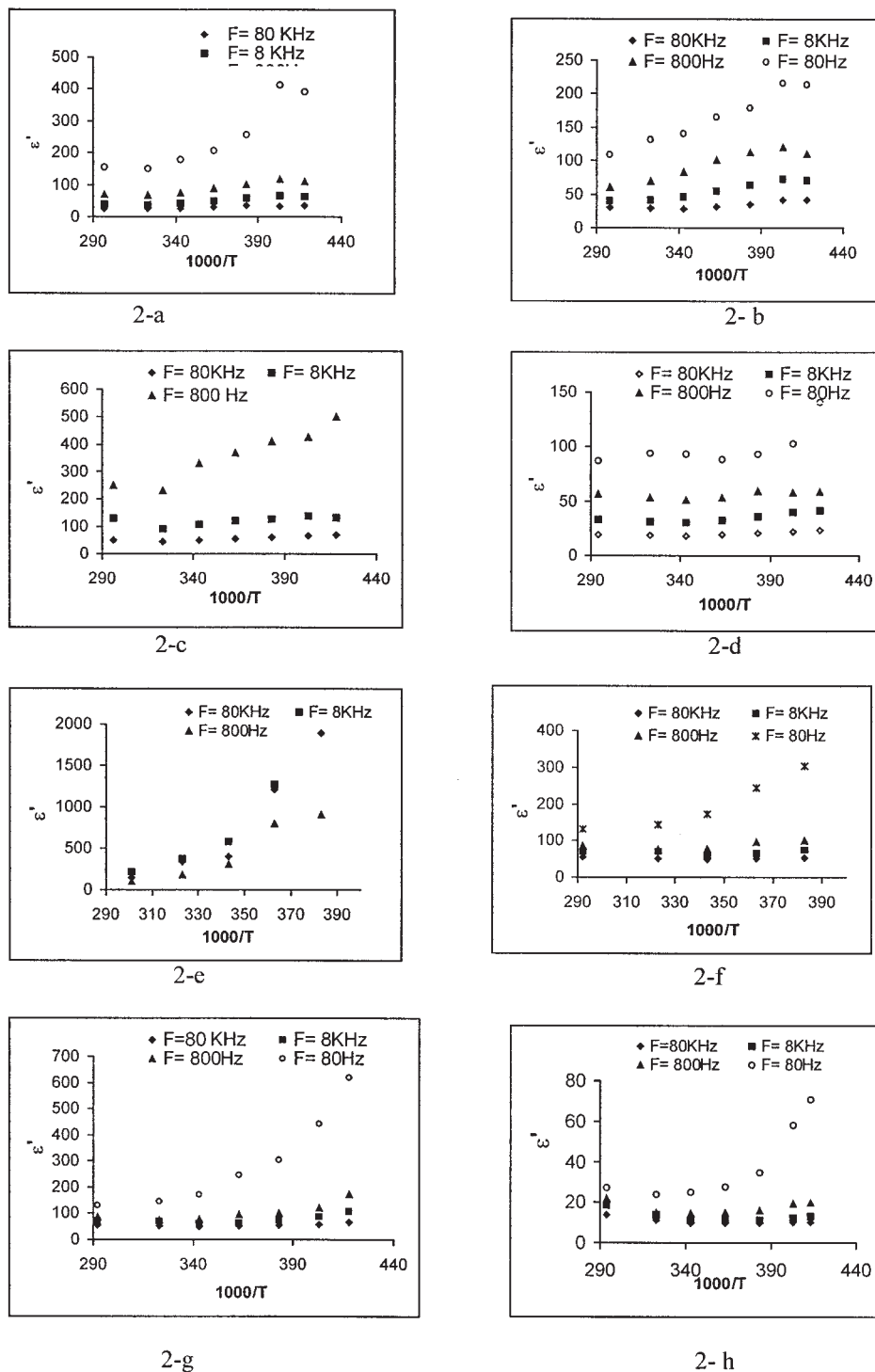Figures 8(a,b) show the effect of ferric chloride concentration—used in preparation—on the dielectric

Figure 2 The temperature dependence of the dielectric constant ε' at some selected frequencies and at different concentrations of ferric chloride (PY : FeCl$_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3(d)) and potassium persulphate (PY : K$_2$S$_2$O$_8$ = 1 : 1.5 (e), 1 : 2 (f), 1 : 2.5 (g), 1 : 3 (h)).

constant and AC conductivity. When the concentration of ferric chloride increases up to the ratio of FeCl$_3$:Py = 2.5:1, the amount of (Cl$^-$) counterions increases, which leads to an increase in DC conductivity and consequently in the polarization (dielectric constant ε') and AC conductivity σ' (since there is a

strong correlation between the different conduction mechanisms and the polarization mechanism,[4,16]). However for molar ratios greater than 2.5:1 there is a competitive incorporation of iron-based counterions (FeCl$_4^-$), which are heavier and larger than (Cl$^-$). They may not contribute to conduction or polarization as
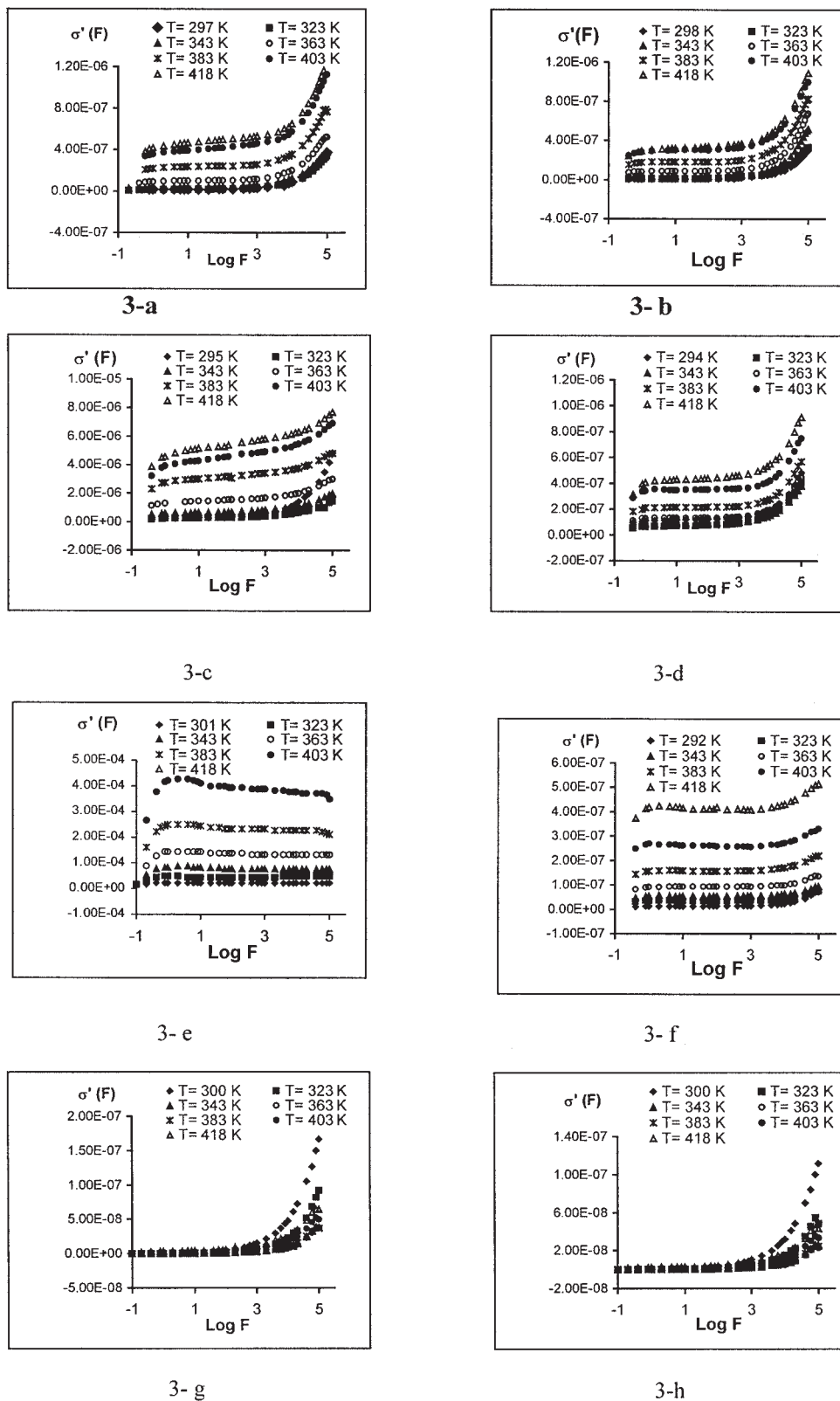
Figure 3   The frequency dependence of the real part of the AC conductivity σ' at different temperatures and at different concentrations of ferric chloride (PY : FeCl$_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : K$_2$S$_2$O$_8$ = 1 : 1.5 (e), 1 : 2 (f), 1 : 2.5 (g), 1 : 3 (h)).

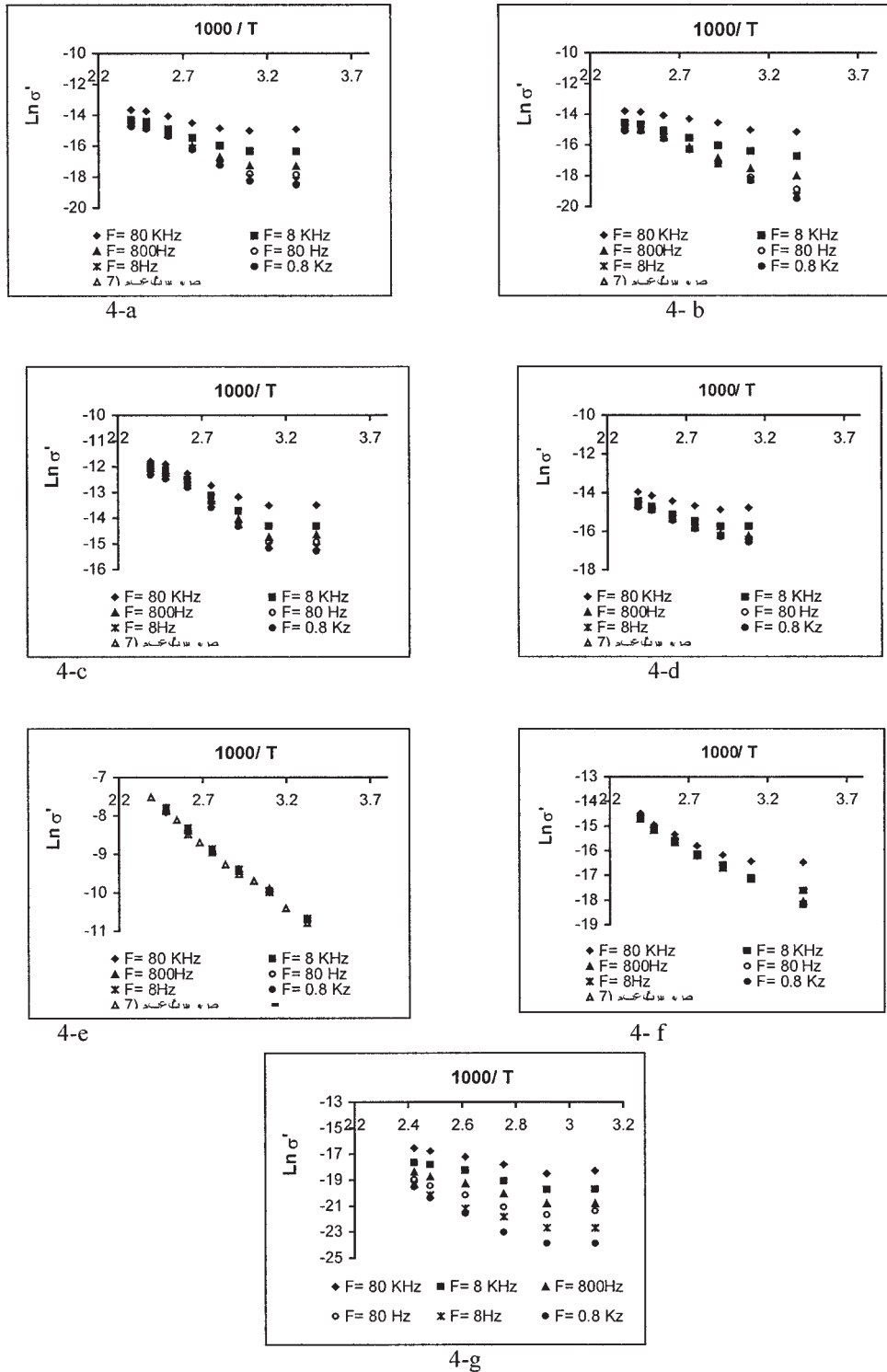**Figure 4** The temperature dependence of the real part of the AC conductivity σ' at some selected frequencies and at different concentrations of ferric chloride (PY : $FeCl_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : $K_2S_2O_8$ = 1 : 2 (e), 1 : 2.5 (f), 1 : 3 (g)).

easily as the lighter ions (Cl^-). Moreover because of the presence of ($FeCl_4^-$) counterions may hinder the motion of charge carriers since an ($FeCl_4^-$) ion represents a higher barrier to be overcome by a hopping

electron. Consequently the polarization in the system is reduced as well as the AC conductivity and tan δ. Figures 8(c) and 8(d) show the effect of potassium persulfate concentration—used in preparation—on
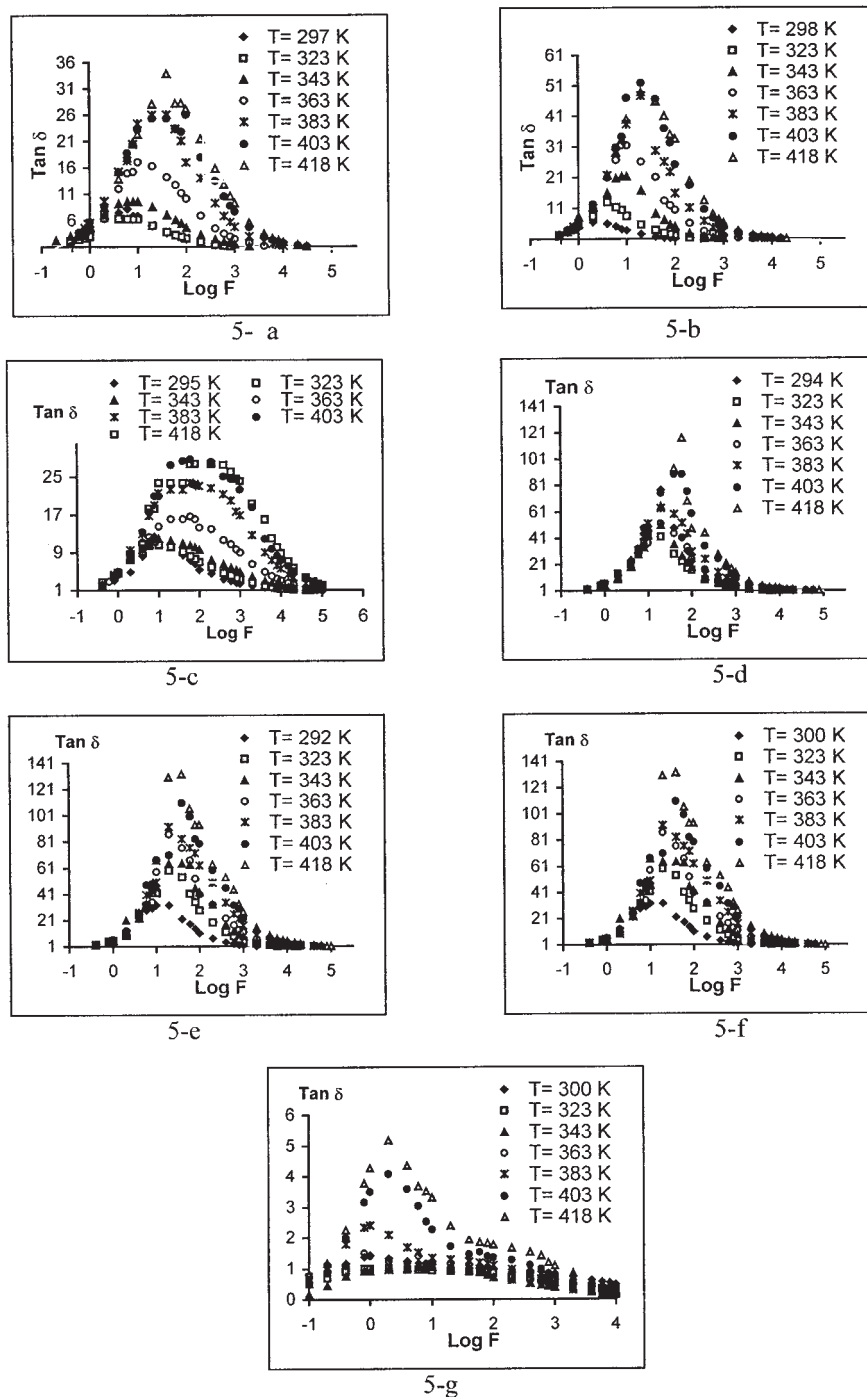
Figure 5 The frequency dependence of the dielectric loss factor "tan δ" at different temperatures and at different concentrations of ferric chloride (PY : $FeCl_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : $K_2S_2O_8$ = 1 : 2 (e), 1 : 2.5 (f), 1 : 3 (g)).

the dielectric constant and AC Conductivity. As mentioned before, it is well known that the increase in the dielectric constant values is mainly due to the interfacial polarization. Therefore, it is expected that we find at low concentrations of $K_2S_2O_8$ the dielectric constant values are higher than those at high concentrations because of the low molecular weight and the small molecules of the

polymer, which may lead to the increase in charge hopping probability and consequently to a greater accumulation of charge carriers on the boundaries increasing the interfacial contribution to polarization. However, at higher concentrations, the molecules are bigger and the formed polymer has higher molecular weight, decreasing the charge transfer probability and the accumulation
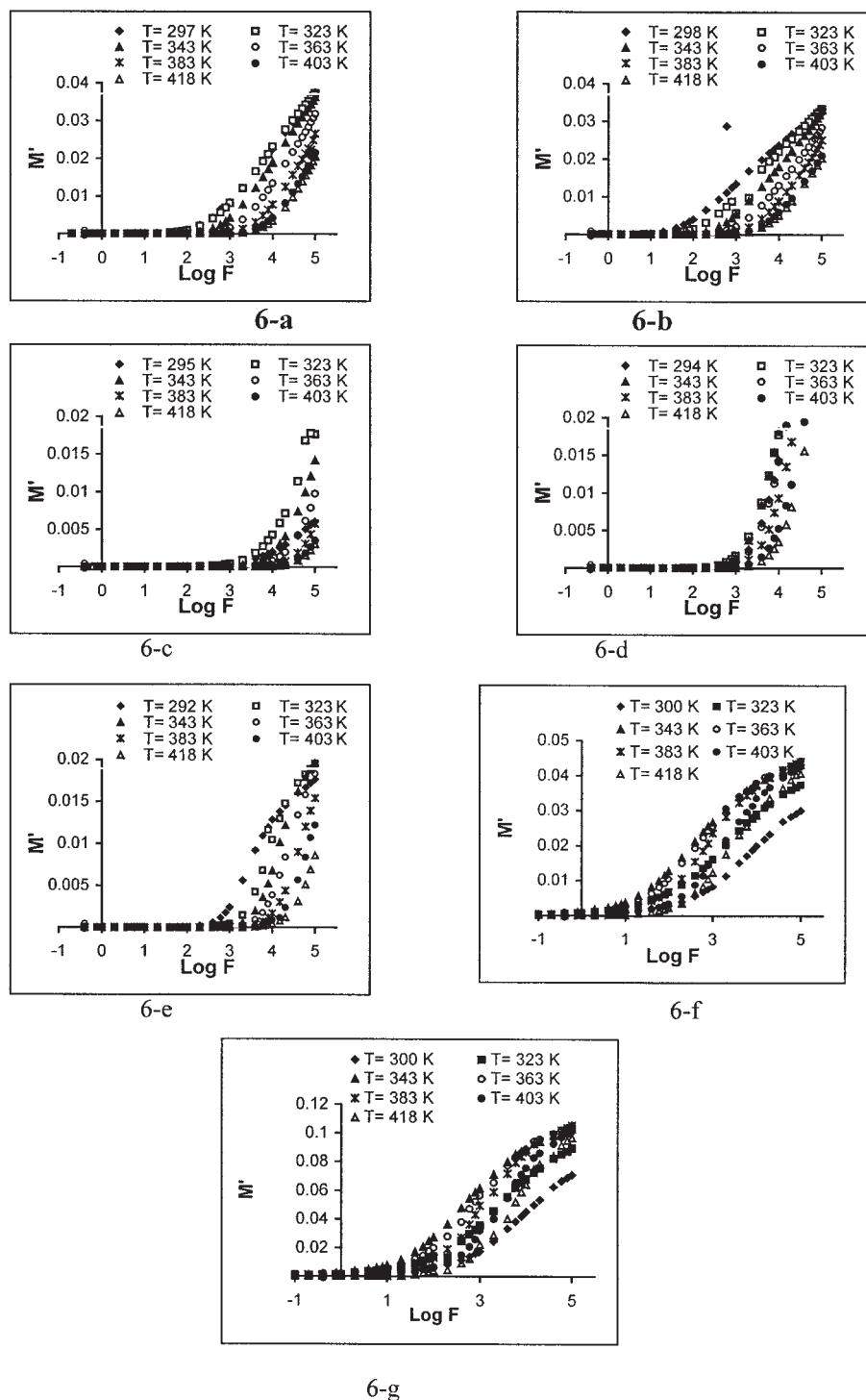
Figure 6 The frequency dependence of the real part of the electric modulus M' at different temperatures and at different concentrations of ferric chloride (PY : FeCl$_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : K$_2$S$_2$O$_8$ = 1 : 2 (e), 1 : 2.5 (f), 1 : 3 (g)).

of charges at the boundaries is reduced leading to a decrease in the dielectric constant values.[17, 18]

CONCLUSIONS

After preparation and drying at 333 K, further heating at constant temperature at (353 K) for 4 days has enhanced

the resistivity of the samples which can be considered as a simple method of obtaining polypyrrole (PPy) in a dielectric state, this may be useful in some future applications such as the manufacture of supercapacitors.

AC conductivity is obviously thermally activated and the suggested charge transport mechanism is via
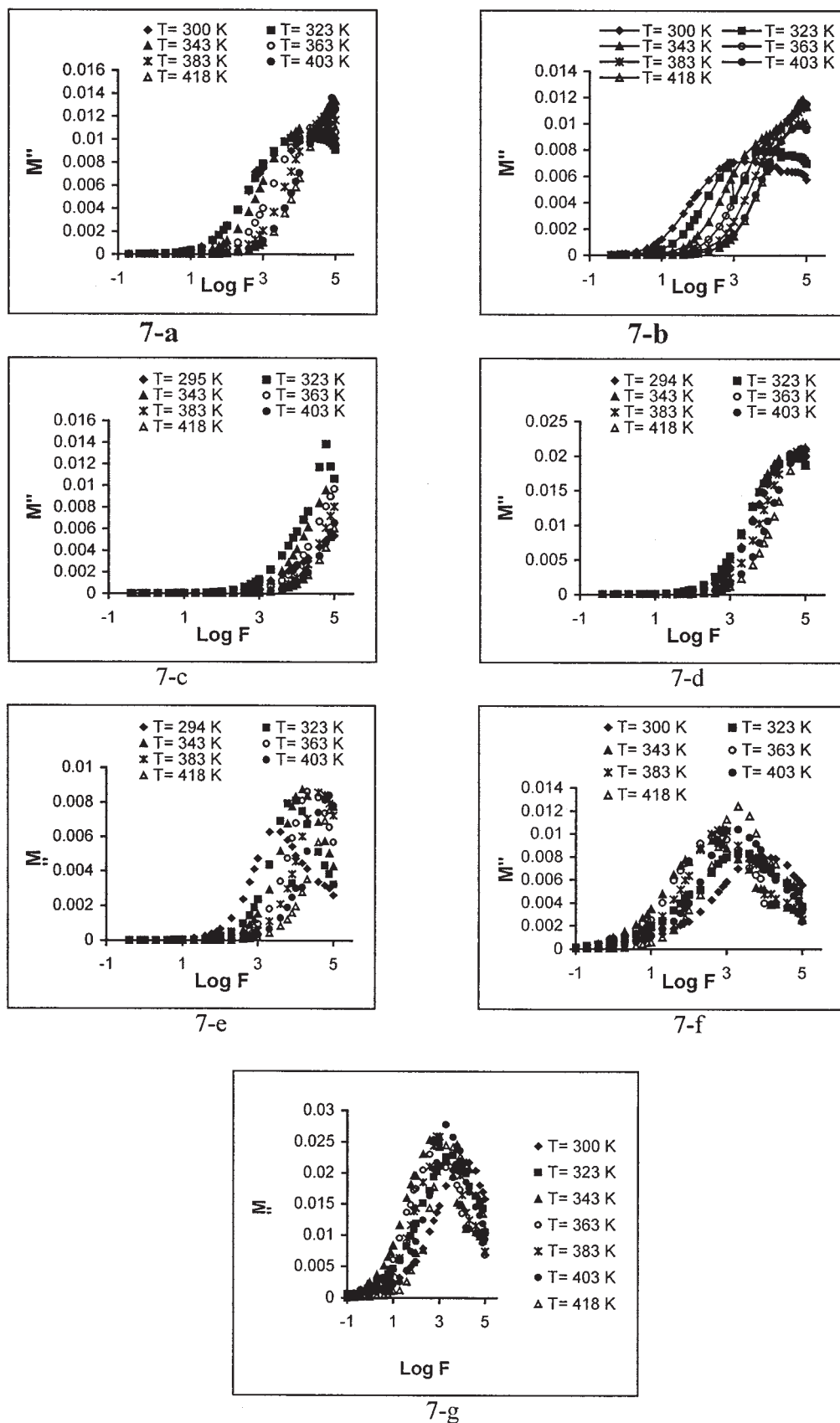
Figure 7 The frequency dependence of the imaginary part of the electric modulus M'' at different temperatures and at different concentrations of ferric chloride (PY : $FeCl_3$ = 1 : 1.5 (a), 1 : 2 (b), 1 : 2.5 (c), 1 : 3 (d)) and potassium persulphate (PY : $K_2S_2O_8$ = 1 : 2 (e), 1 : 2.5 (f), 1 : 3 (g)).
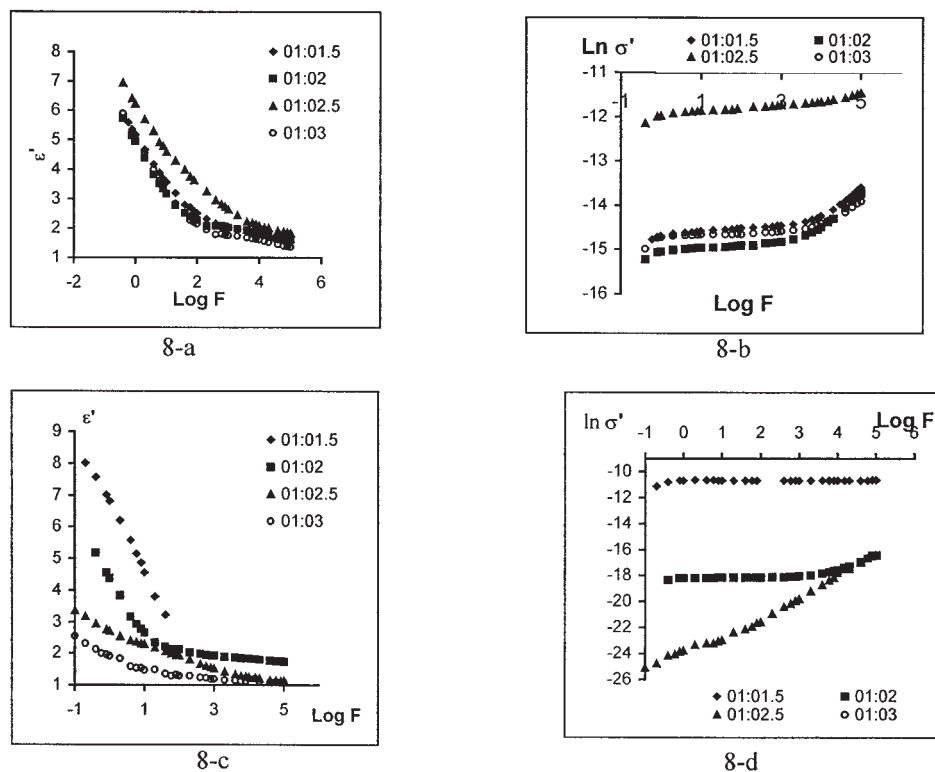
Figure 8 The effects of ferric chloride concentration (a,b) and potassium persulphate concentration (c,d) on the dielectric constant ε' and AC conductivity σ'.

π-electron, this is confirmed by the shift in tan δ peaks towards higher temperatures.

The concentration of the oxidizing agents has a considerable effect on the electrical properties of PPy. The sample prepared using the ratio of Py : $K_2S_2O_8 = 1 : 1.5$ shows a frequency independence of the conductivity, which makes this sample a good candidate for manufacturing of resistors.

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