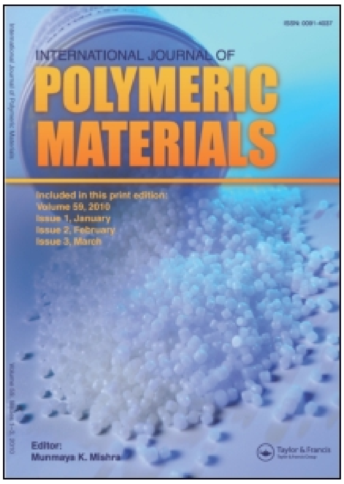

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S. Abdul Jawad[a]; A. Alnajjar[a]; M. Bader[b]
[a] Physics Department, P.O. Box 17551 Al-Ain, UAE University, United Arab Emirates [b] Chemistry Department, P.O. Box 17551, Al-Ain, UAE University, United Arab Emirates

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Dielectric Spectroscopy of Pure and KBr Dispersed Polypyrrole

S. ABDUL JAWAD[a],*, A. ALNAJJAR[a] and M. BADER[b]

[a]*Physics Department, P.O. Box 17551 Al-Ain, UAE University, United Arab Emirates;* [b]*Chemistry Department, P.O. Box 17551, Al-Ain, UAE University*

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The effect of frequency at room temperature of the ac impedance, permittivity and electric modulus of pure Polypyrrole and KBr Polypyrrole powders with different ratios was investigated in the frequency range 0.1 Hz. to 10^6 Hz. The frequency dependence of the ac impedance is similar to that observed in RC network in parallel. The real component of ac impedance is frequency independent in low frequency range and becomes proportional to the inverse of frequency at high frequency range. The equivalent bulk resistance decreases with increasing the KBr content while the equivalent capacitance remains nearly unchanged. The relaxation transition in KBr dispersed Polypyrrole is assigned to a summation of relaxations occurring within the bulk.

Keywords: Impedance; resistivity; relaxation; dielectric; impedance; modulus

1. INTRODUCTION

The relationship between the structure of pure and doped Polypyrrole and electrical conductivity has been the subject of intensive study in recent years [1, 2], it has been proposed that Polypyrrole can exist in an aromatic form and quinord form, and that the former corresponds to the undoped state and the latter to the doped state [3, 4, 5]. In addition the study of NMR spectroscopy reveals that at room temperature the electric conductivity is mainly due to the hopping conduction mechanism for pure Polypyrrole [6]. However, Drude metallic response was suggested for doped Polypyrrole [2, 7].

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*To whom correspondence should be addressed.

In this paper we report the ac behavior of pure and KBr dispersed Polypyrrole. The ac behavior will be discussed in terms of three electrical quantities, namely, impedance, permittivity and electric modulus. The effect of KBr content on the electrical behavior of Polypyrrole will be discussed.

2. EXPERIMENTAL

2.1. Materials

Pyrrole was purchased from Fluka Chemicals and was used as received. The electrochemical polymerization was performed in a one-compartment cell with two platinum wires as the working and the counter-electrode and a sodium saturated calomel electrode (SSCE) as the reference electrode. Typically, a reaction vessel contained 0.05 M monomer and 0.1 M H_2SO_4 or 0.1 M $LiClO_4$ in acetonitrile solvent. The solution containing electrolyte and monomer was purged with nitrogen for about 30 min. before polymerization. The resulting polymer was washed with water and acetone and dried in a vacuum oven for 24 hrs. The samples for measurements were prepared by crushing KBr crystals with Polypyrrole at different wt/wt ratios to obtain the powder mixtures. The total weight of all the samples was kept constant at 0.1 gm. The prepared crushed powders were then pressed into pellets of 1 cm diameter and ~ 0.8 mm thick using an IR press.

2.2. AC Impedance Measurements

The ac-impedance were carried out at room temperature in the frequency range 0.1 Hz to 10^6 Hz., using a Solarton-1260 impedance/Gain phase Analyser (Shlumberger Instrument). The apparatus is controlled by Z-60 and Z-View packages which maximize the performance and data handling of the system. The measurements were performed on a disc-shaped sample of 1 cm diameter and about 0.8 mm thick. Carefully applied graphite electrodes with identical surface area for all samples were add-on to each surface, so the disc is fully sandwiched between two copper parallel plates. The sample setup was then kept in a shielded cavity to improve low frequency measurements.

Best signal generate amplitude was selected after performing a series of amplitude sweeping tests. The experimental measurements were performed at zero dc bias. Using this setup, the complex impedance and phase angle were determined. From those measurements the real and imaginary components of impedance, permittivity and electric modulus were determined. In order to eliminate the dimensional effects on ac impedance data the contact surface areas for all specimens were kept constant and the data were reported in the units of ohm/cm.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of the phase angle (θ) and the real component (Z') of ac impedance with frequency respectively. The general feature of these curves is similar to that observed for RC network in parallel. The phase angle for pure Polypyrrole varies from nearly -90 at 10^6 Hz. to almost 0 at 0.1 Hz. indicating that the resistive component of the equivalent circuit is dominant at low frequencies and the capacitive component is dominant at high frequencies. Adding KBr to pure Polypyrrole results in an increase of the phase angle at high frequencies range which attains a value of $-75°$ at 10^6 Hz without showing any plateau region in the high frequencies range. On the other hand, the real component of ac impedance (Z') is independent of frequency at low frequencies range showing a plateau region. The frequency range of this plateau region increases with increasing the KBr content and extends from 0.1 Hz. to 10^4 Hz. for 50/50 PP/KBr. At high frequencies range Z' for both pure Polypyrrole and KBr dispersed polypyrrole becomes proportional to the inverse of frequency. Therefore, the bulk material can be represented by RC network in parallel as stated above, hence, ac impedance can be written as a complex quantity,

$$Z^* = Z' + jZ'' \tag{1}$$

where Z' and Z'' are the real and imaginary components of complex ac impedance (Z^*) and $j = \sqrt{-1}$.

The analysis of the RC networks in parallel yields the following relations [8,9]

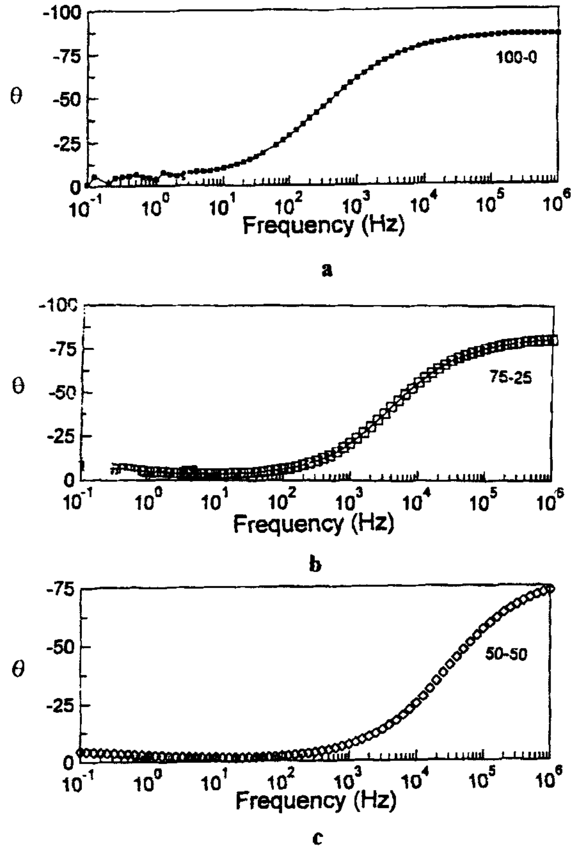


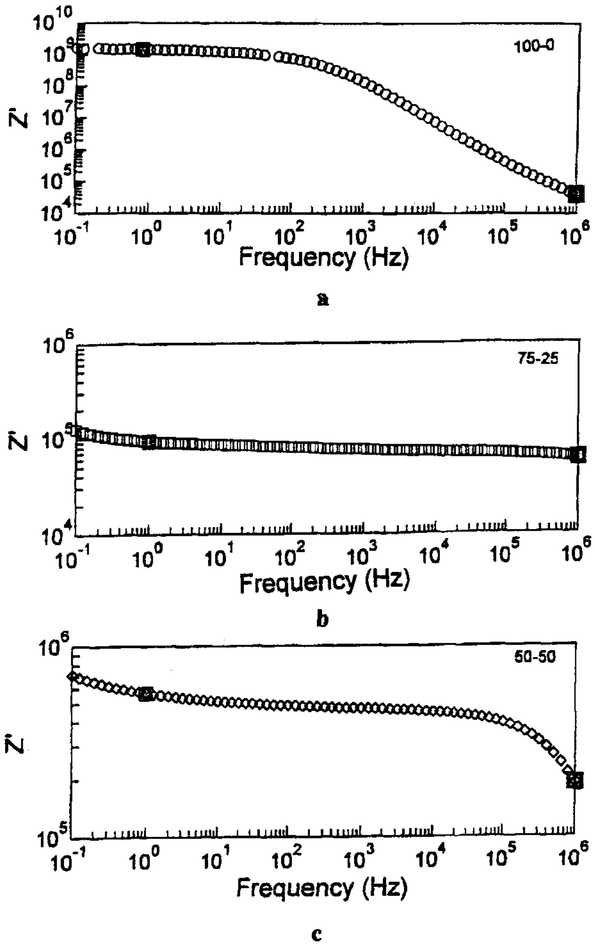
FIGURE 1 Phase angle (θ) versus frequency for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

$$Z' = R/1 + (\omega\ RC)^2 \tag{2}$$

$$Z'' = R^2\ C/1 + (\omega\ RC)^2 \tag{3}$$

where ω is the angular frequency ($2\pi f$).

The plot of Z'' vs. Z' yields a semi-circle of radius R/2 and maximum value of Z'' defined by $\omega\ \tau = RC = 1$, where τ is the relaxation time.



a

b

c

FIGURE 2 Imaginary component of AC impedance (Z') ohm/cm vs. frequency for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

The real and imaginary components of complex permittivity can be determined from the following relations in terms of Z' and Z'',

$$\varepsilon' = Z''/(Z'^2 + Z''^2)\omega C_0 \tag{4}$$

$$\varepsilon'' = Z'/(Z'^2 + Z''^2)\omega C_0 \tag{5}$$

where C_0 is the dielectric constant of free space.

However, the dielectric constant permittivity, is a compliance. As in the case of a mechanical compliance it can be inverted to give an electric modulus (M) where,

$$M^* = \varepsilon^{*-1} = M' + j\,M'' = (\varepsilon' - j\,\varepsilon'')^{-1} \tag{6}$$

then,

$$M' = \varepsilon'/\varepsilon'^2 + \varepsilon''^2 \tag{7}$$

$$M'' = \varepsilon''/\varepsilon'^2 + \varepsilon''^2 \tag{8}$$

Using ac impedance analysis [10,11] it is possible to identify the various regions of the sample, where an equivalent circuit consisting from R and C elements represent the grain boundary, the bulk and electrode regions. These regions might appear as a series of semicircles in the plot of the imaginary and the real components of ac impedance. However, the study of relaxation transitions of polymers using the electric modulus has two advantages over the loss factor ε'', first the maximum in M'' will occur at a lower temperature than the maximum in ε'', second, since ε' appears in M'' equation in the denominator to the second power, its tendency to overwhelm the loss factor is minimized.

Figure 3 and 4 show the variation of Z'' and M'' with frequency respectively. A well defined relaxation peak was observed in pure and KBr dispersed Polypyrrole. It is clear that the relaxation peak in M'' and Z'' spectra are broader than Debye peak and the frequencies of the peak maxima in the two spectra do not coincide. The broad peak in Z'' and M'' spectra can be assigned to a summation of relaxation occurring within the bulk material. Nevertheless, the peak maximum moves to a higher frequency with increasing the content of KBr. The complex impedance plane plot (Z'' vs. Z') as shown in Figure 5 for pure Polypyrrole gives a distorted semi-circle, with a tail which can be used to construct a small circle at low frequency regions in the KBr dispersed Polypyrrole samples. The calculated relaxation time can be determined from the semi-circle using the formula $\omega\tau = 1$. The calculated values of τ and the equivalent bulk resistance and capacitance of pure and dispersed KBr Polypyrrole are given in Table I. The calculated relaxation time decreases dramatically with increasing KBr

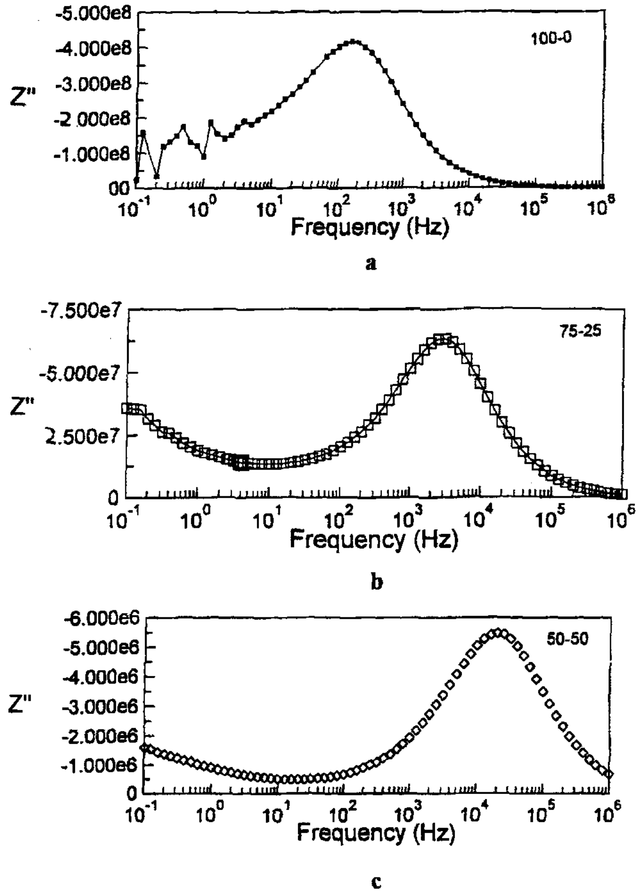


FIGURE 3 Imaginary component of ac impedance (Z'') versus frequency for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

content, this decrease is associated with a decrease in the equivalent resistance of the bulk (R). Indicating that adding KBr increases the conductivity of the Polypyrrole. This increase in resistivity with increasing the KBr content could be due to the strong ion-dipole interaction which would result in the generation of large free volume in the host polymer and consequently the increase of the mobility of charge carriers within the bulk.

The observed broad peak and the semi-circles in the complex plane plot indicate that the relaxation process is due to the rotational

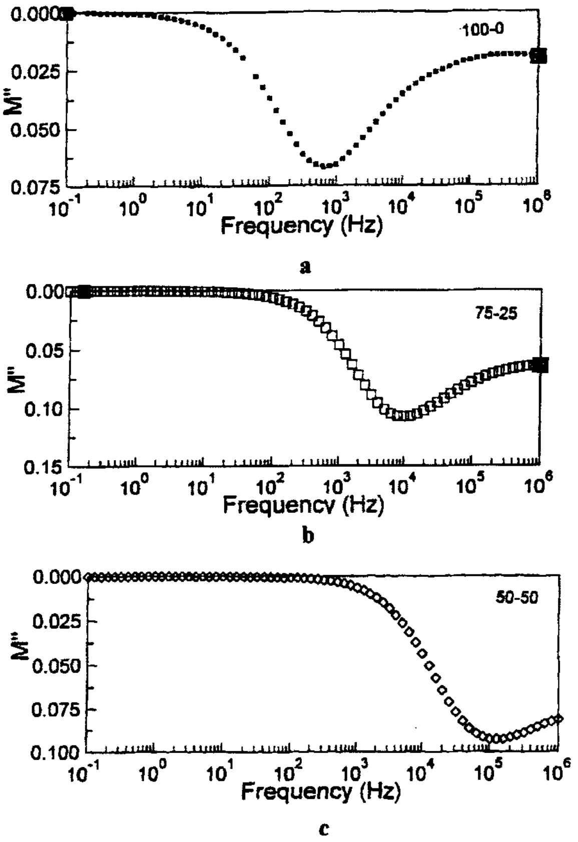


FIGURE 4 Imaginary component of electric modulus (M'') versus frequency for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

motion of identical Pyrrole rings around the single bond, from the grain boundaries between the crystals and with a possibility that it could be a result of the imbedded interfaces where the relaxation process occurs depends on the size and properties of the two phases. On the other hand, adding KBr to Polypyrrole introduces high electrostatic interactions between the chains and ions with a possibility of forming hydrogen bonding between the Pyrrole rings and moisture, knowing that KBr is highly hygroscopic material. Therefore, it is expected that mobility of K and Br ions and the Pyrrole ring will be reduced due to electrostatic interactions, dipole interactions and H-bonding between the hydrogen atom on the nitrogen and moisture,

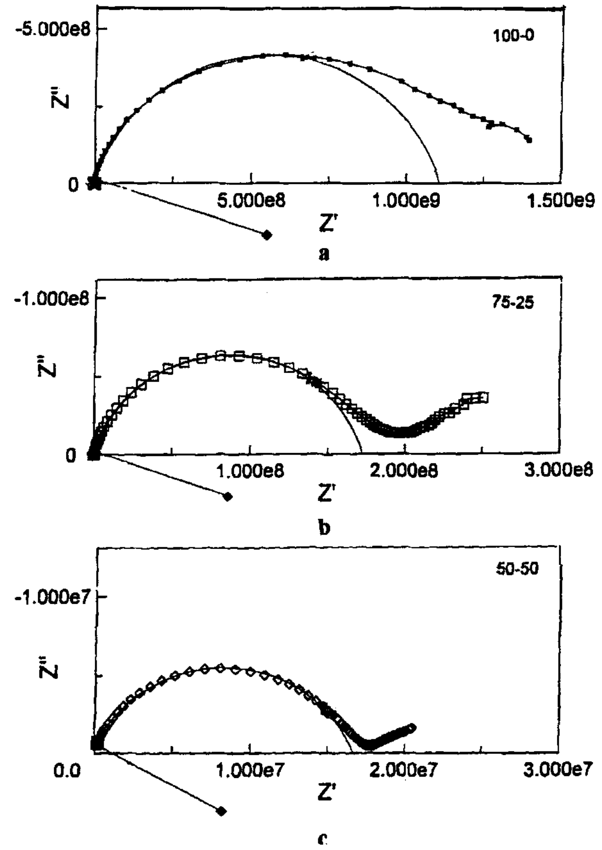


FIGURE 5 Imaginary component (Z'') versus real component (Z') for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

as a result these interactions will make the rotation around the single bond more difficult as the relaxation peak moves to a higher frequency. Nevertheless, the relaxation process peak was not observed in the plot of ε'' with frequency due to the effect of dc ionic conductivity which increase at low frequencies and consequently masks any relaxation transition peak. On the other hand the dramatic increase in ε' as shown in Figure 6 at low frequency range may be due to space charge contribution which depends on the purity and perfection of crystal, in addition to the dc conductivity which is dominant at low frequency region.

TABLE I Equivalent Resistance (R ohm), Equivalent Capacitance (C F), Relaxation time (τ sec.) and maximum angular frequency (ω)

Sample	*R (ohm)*	*C (F)*	*τ (m sec)*	*ω*
100/0	1.11×10^{9}	7.4×10^{-13}	0.858	1165
75/25	1.7×10^{8}	3.1×10^{-13}	0.0565	1.77×10^{4}
50/50	1.69×10^{7}	4.5×10^{-13}	0.00855	1.197×10^{5}

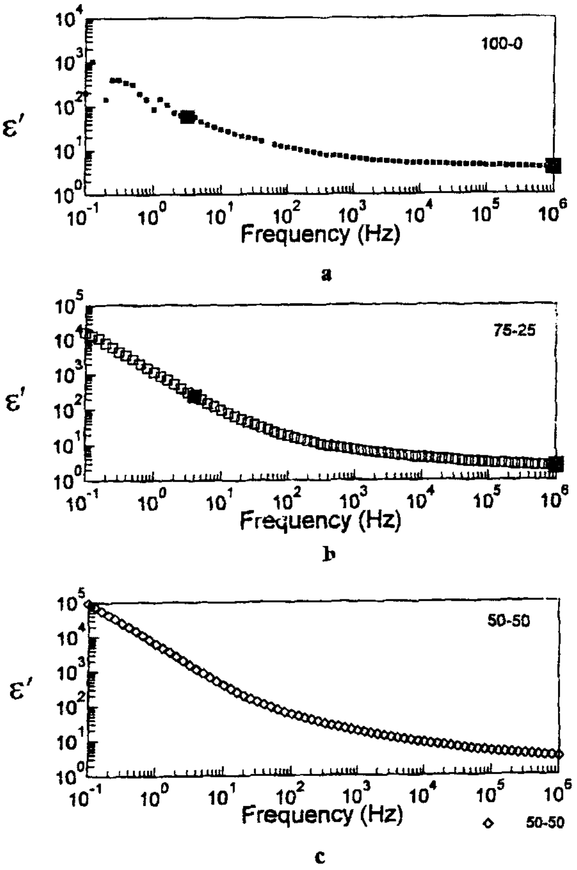


FIGURE 6 Real component of dielectric constant (ε') versus frequency for KBr dispersed Polypyrrole at different ratios (Polypyrrole-KBr).

4. CONCLUSIONS

The dielectric study of pure Polypyrrole and KBr dispersed Polypyrrole at room temperature in the frequency range 0.1 Hz to 10^6 Hz reveals the following conclusions:

1. The resistivity of the bulk material is nearly independent of frequency in the low frequency range, this range of independence increases with increasing the KBr content.
2. The observed relaxation in pure Polypyrrole is due to a local rotational motion of identical Pyrrole rings around a single bond. Adding KBr to Polypyrrole introduces high electrostatic interactions which hinder the rotation of the Pyrrole rings and as a result the relaxation peaks move to higher frequencies.
3. The plot of complex plane of Z'' vs. Z' indicates the existence of two relaxation mechanisms. These are mainly due to the dipole rotation and the grain boundaries between the crystals.

Acknowledgements

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