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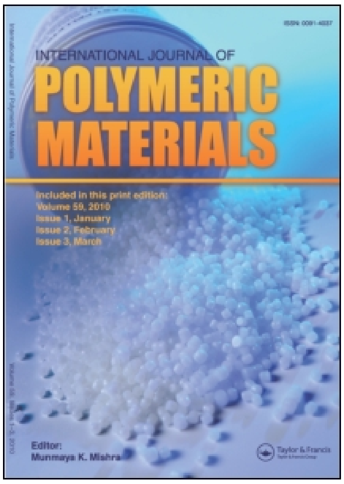

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Dielectric Spectroscopy of Polycarbosilazane-based $CuCl_2$ Metallopolymers

I. M. Arafa[a]; H. M. El-Ghanem[b]; A. B. Hallak[c]; S. Abdul Jawad[c]
[a] Department of Applied Chemistry, Faculty of Sciences and Arts, Jordan University of Science and Technology, Irbid, Jordan [b] Department of Physics, Faculty of Sciences and Arts, Jordan University of Science and Technology, Irbid, Jordan [c] Department of Physics, The Hashemite University, Faculty of Sciences and Arts, Zarqa, Jordan

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I. M. Arafa
Department of Applied Chemistry, Faculty of Sciences and Arts,
Jordan University of Science and Technology, Irbid, Jordan

H. M. El-Ghanem
Department of Physics, Faculty of Sciences and Arts,
Jordan University of Science and Technology, Irbid, Jordan

A. B. Hallak
S. Abdul Jawad
Department of Physics, The Hashemite University,
Faculty of Sciences and Arts, Zarqa, Jordan

A series of poly (carbosilazane-$CuCl_2$) metallopolymers was prepared by the reaction of varying amounts (5% to 30%) of anhydrous $CuCl_2$ with polycarbosilazane, $[-(CH_3)_2SiNH(CH_2)_2NH-]_n$, matrix in tetrahydrofuran under continuous sonication. Dielectric measurements were performed at room temperature (25°C) in the frequency range 1 Hz to 10^6 Hz. It was found that the ac conductivity increases with increasing the $CuCl_2$ up to 16% and then starts to dramatically decrease. The results reveal that all the dielectric parameters such as ac impedance, dielectric permittivity, and electric modulus behave similar to that observed in ac conductivity. (i.e., maximum or minimum depends on the considered dielectric parameter). It is suggested that at low concentration of metal content, all the $CuCl_2$ is uniformly bound to the backbone of the polymer chains, where the conduction mechanism in the system is by electrons jumping (carrier hopping between the chains), whereas at high metal content the coordination capacity of the backbone is exceeded and $CuCl_2$ is present as molecular clusters that lead to an increase in the interaction distances, and make hopping between chains more difficult, and hence, resulting in a reduction of conductivity.

Keywords: polycarbosilazane, metallopolymer, organosilicon polymer, dielecirc permittivity, electric modulus, relaxation transition

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Address correspondence to H. M. El-Ghanem, Department of Physics, Faculty of Sciences and Arts, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan. E-mail: hmel@just.edu.jo

INTRODUCTION

The past few years have witnessed an increasing interest in metallomesogenes, metallopolymers, and other metal-containing macromolecules [1–11]. This interest stems from their potential applications in modern technology such as liquid crystals, electrical, optical, opto-electronic, ferroelectric, ferromagnetic, as well as catalysis [1–6]. The incorporation of metal ions, complexes, and clusters in macromolecular systems is reported to produce significant changes in their structures and properties. In these materials the metal center is chemically attached to the surface of the polymer via σ or π bonds at regular inter-spaces or randomly dispersed in the polymeric matrix [1–6]. The former class provides a unique macromolecular system to study numerous electronic processes. Such systems carry many advantages; they can be prepared in a variety of structures and can be structurally modified to be tuned to the desired property. In addition they can be formulated as thin films, fibers, and membranes at relatively low temperatures.

In a series of articles, the present authors have shown that different divalent, trivalent, and mixed valence transition metals can be covalently attached to polycarbosilazane-containing diamino groups such as $[-(CH_3)_2SiNH(CH_2)_2NH-]_n$, PDMSEN [12–14]. In this system, the backbone structure is composed of alternating carbosilazane units. The present article reports on the dielectric behavior of PDMSEN containing varying amounts of $CuCl_2$, in the frequency range 1 Hz to 10^6 Hz. Different dielectric parameters will be discussed such as ac conductivity, permittivity, loss factor, impedance, and electric modulus. It is important to note that some applications for metallopolymers require materials with well-separated metal sites (low metal content) whereas others need agglomerated metal clusters (high metal contents).

EXPERIMENTAL

Materials

All chemicals and solvents were reagent grade and used as received without further purification unless otherwise stated [$(CH_3)_2SiCl_2$ (99%, Acros), ethylenediamine, (99%, Janssen Chimica), $CuCl_2$, (Merck) and triethylamine (98%, Scharlau)].

Synthesis of $[-Si(CH_3)_2NHCH_2CH_2NH-]_n$ Matrix (PDMSEN)

The general method used to produce $[-Si(CH_3)_2NHCH_2CH_2NH-]_n$ polymer was previously described [12–16]. In this method, equimolar amounts of $(CH_3)_2SiCl_2$ and $H_2NCH_2CH_2NH_2$ in toluene in the presence of Et_3N were refluxed under nitrogen for 4–5 h. The product was isolated from toluene under reduced pressure to yield a creamy-waxy solid. The average molecular weight (M_n) was found to be 2300 g/mole, n = 20 (vapor pressure osmometry, benzene, 35°C).

Incorporation of $CuCl_2$ into the PDMSEN Matrix

These metallopolymers were prepared in THF using different wt/wt ratios of $CuCl_2$ and PDMSEN (5%, 10%, 16%, 20%, 26%, and 30%). In general, the $CuCl_2$ and PDMSEN were separately dissolved in THF and mixed in a round-bottom flask. The reaction mixture was subjected to heating (70–75°C for 2 h) in a sonicating bath. The yellow–light green products were precipitated by the addition of hexane, filtered off and eventually dried under vacuum at room temperature for several hours.

X-Ray Diffraction

Powder X-ray diffraction (XRD) was performed using a PW 1729 Philips diffractometer interfaced with a computer control unit model PW 1710 using copper source (K_α radiation, $\lambda = 1.54\,\text{Å}$). The diffraction patterns were recorded using a PM 8203 A one line recorder. The angular range of 2θ was taken between 3° and 80° because no peaks were observed below 3° for all samples. The scanning speed of the diffractometer was in 0.02°–0.04° (2θ/s) depending on the quality of signal–to-noise ratio. The positions of the peaks were determined by curve-fitting procedure of the experimental XRD data using Table Curve-2D software (Lowess Algorithm).

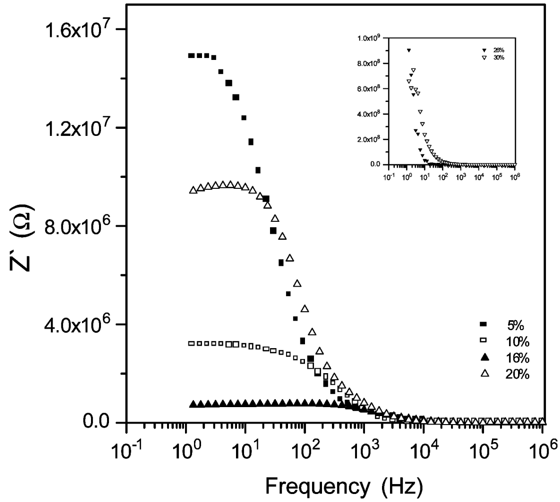
AC Measurements

Samples of PDMSEN—containing different concentrations of $CuCl_2$ (5% to 30%), about 0.2 g of very fine powder—were compressed at $10\,\text{ton.cm}^{-2}$ for 10 min forming circular discs 13 mm in diameter and varied thickness between 0.5 to 1 mm. A silver coating was applied to each surface of the disc. Then it was sandwiched between two brass circular discs to ensure good ohmic contacts with brass electrodes.

The ac measurements were performed in the frequency range between 1 Hz and 10^6 Hz at room temperature using a 1260 Impedance Gain Phase Analyzer (Solarton Analytical). The system was controlled using the Z–60 and Z-View Packages, which maximize the performance and data handling of the system. The generator amplitude was kept at 0.5 rms volts and 0 dc bias. The complex ac impedance and the phase angle were measured, while the real and imaginary components of dielectric constant, impedance, electric modulus were calculated [15].

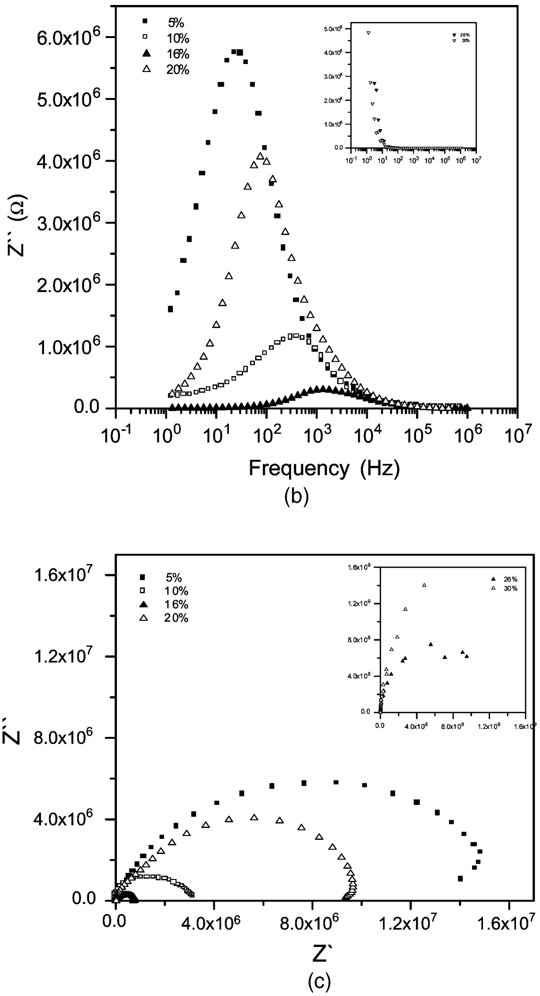
RESULTS AND DISCUSSION

Figures 1a and 1b show the dependence of the real and imaginary components of ac impedance on frequency at zero dc bias for different concentrations of $CuCl_2$. The general features for the samples containing 5%, 10%, and 16%, are similar to that observed for RC-network in parallel. At low frequencies, the real component of ac impedance (Z′) is nearly independent of frequency and attains a minimum value for the sample containing 16% of $CuCl_2$, indicating that this sample possesses the highest conductivity. In the frequency range between 10 Hz and 1 kHz, a sharp drop in the real component of ac impedance was observed for all samples with a well-defined relaxation peak in the plot of the imaginary component of ac impedance especially for samples containing 5% to 20% of $CuCl_2$, as shown in Figure 1b. However, the intensity of the peaks decreases with increasing amounts of $CuCl_2$,



(a)

FIGURE 1 (a) Real (Z′) component of impedance versus frequency for polycarbosilazane-based $CuCl_2$. (b) Imaginary component (Z″) of impedance versus frequency for polycarbosilazane-based $CuCl_2$. (c) Real (Z′) versus imaginary (Z″) of impedance for polycarbosilazane-based $CuCl_2$.



(b)

(c)

FIGURE 1 Continued.

and moves to higher frequency. For the sample that contains 20% CuCl$_2$, the intensity of the peak starts to increase and moves to a lower frequency. The peak completely disappears in the samples that contain 26% and 30% of CuCl$_2$. The plot of the real component (Z′) versus imaginary component (Z″) is shown in Figure 1c. Nearly perfect semi-circles were observed in the samples that contain 5%, 10%, and 16%, and some distortion in the semi-circles was detected in the sample containing 20%. For high concentrations that is, 26% and 30%, no semi-circles were detected. The radius of the semicircles in the plot of Z′ versus Z″ represent the bulk resistance (R), where the conductivity (σ) can be determined using the relation,

$$\sigma = L/RA$$

where L is the sample thickness, and A is the sample area.

The calculated values of conductivity are shown in Figure 2. The conductivity increases with increasing $CuCl_2$ content up to about 16% and attaining a maximum value of $3.6 \times 10^{-6} (\Omega.m)^{-1}$. Then it starts to decrease to a value of $3 \times 10^{-9} (\Omega.m)^{-1}$ for the sample that contains 30%. The incorporation of anhydrous $CuCl_2$ into $[-(CH_3)_2SiNH(CH_2)_2NH-]_n$ matrix was performed using a typical literature procedure in a THF solution in a sonicating bath, as shown in Scheme 1 [12].

It is well established that the structure of PDMSEN chain is linear, and is composed of alternating $(CH_3)_2SiNHCH_2CH_2NH-]$ carbosilazane units with strong affinity for binding transition metal ions [12, 14, 16]. However, the maximum capacity of such material to hold metal ions is dictated by the number of binding sites on its surface. At low metal content, all the $CuCl_2$ is uniformly bound to the backbone and therefore the metal sites are separated by insulating barriers at regular inter-spatial distances. Consequently, conduction through a single type of structure is expected. At 16% all the binding sites are occupied where the conductivity attains its maximum value. By

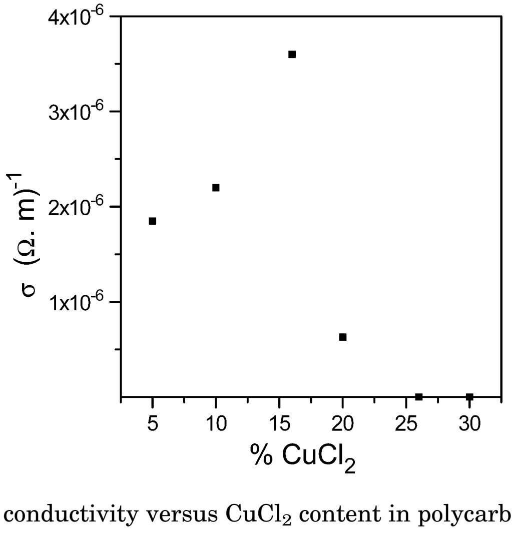
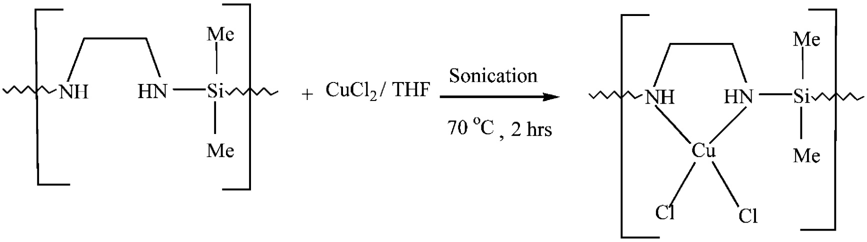


FIGURE 2 AC conductivity versus $CuCl_2$ content in polycarbosilazane-based $CuCl_2$.



SCHEME 1 Incorporation of $CuCl_2$ in polycarbosilazane polymer.

increasing the metal content the coordination capacity of the backbone is exceeded. Therefore, two possibilities may arise, after the chains hold their maximum capacity, the excess $CuCl_2$ aggregates/clusters will be physically entrapped in the entire matrix. In this case two structural forms of $CuCl_2$ coexist and consequently, two conduction mechanisms operate at higher metal conent. Alternatively, aggregates/clusters of $CuCl_2$ are held covalently at diamino groups of the carbosilazane backbone to form a different macromolecular structure and eventually one conduction regime operates. It is important to point out that sonication of the reacting mixture assists in obtaining uniform particle size distribution and inter-particle spacing. Information about the packing of PDMSEN chains and $CuCl_2$ clustering was obtained from powder XRD data. The powder X-ray diffraction (XRD) profiles for the PDMSEN matrix, pure $CuCl_2$ and all the PDMSEN-$CuCl_2$ systems are shown in Figure 3. Each XRD pattern of the PDMSEN matrix contains three broad peaks ($2\theta = 8.00°$, $14.95°$, and $28.50°$), which demonstrates that it is predominantly amorphous in nature with small crystalline regions. The average chain-chain distance in PDMSEN was estimated from the main broad peak centered at $2\theta = 14.95°$ using Bragg's law ($n\lambda = 2d \sin\theta$) and found to be 6.88 Å [17, 18, 19]. Examination of the XRD patterns of these PDMSEN-$CuCl_2$ macromolecules show that they are composed of two diffraction sets, the broad peaks of the PDMSEN amorphous phase and a set of sharp peaks due to the crystalline phase of the coordinated $CuCl_2$. In fact, at low $CuCl_2$ concentration (below 20%) the diffraction patterns demonstrate that all $CuCl_2$ are chemically attached to the PDMSEN matrix and therefore exhibit a diffraction peaks different from that of pure $CuCl_2$. However, the XRD profiles of PDMSEN-$CuCl_2$ containing high concentration of $CuCl_2$ (above 20%) display an additional set of diffraction peaks that correspond to fine $CuCl_2$ clusters. Moreover, the shift in the position of the main broad peak of the PDMSEN matrix ($2\theta = 14.95°$) to lower 2θ values

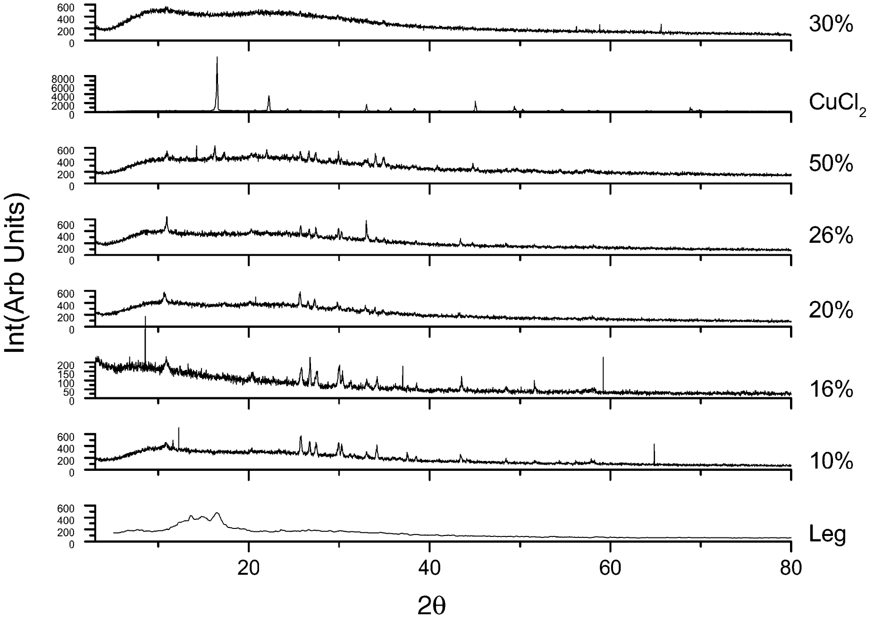


FIGURE 3 Powder X-ray diffraction for PDMSEN matrix, pure $CuCl_2$ crystalline and all PDMSEN -$CuCl_2$ macromolecules.

provide a strong evidence for an increase in the chain-chain distances in all PDMSEN-Cu chloride macromolecules as given in Table 1. This clearly suggests that the $CuCl_2$ is incorporated between the PDMSEN chains and therefore has caused chain-chain expansion to different extents depending on the amounts of $CuCl_2$ introduced. It is interesting to note that chain-chain separation systematically increased from 6.880 Å (PDMSEN) to 8.266 Å (20% $CuCl_2$) then became practically constant as $CuCl_2$% increased from 26 to 50%. This observation can be explained on the basis of the proposition that the inserted $CuCl_2$ into the PDMSEN matrix has caused an increase in the chain-chain separation up to a certain concentration (20% $CuCl_2$) above which $CuCl_2$ tends to form aggregates of fine $CuCl_2$ clusters filling the voids between PDMSEN chains (percolation). It is important to emphasize that at higher concentration (above 20%) sharp peaks due to pure $CuCl_2$ crystallites are observed. The relative amounts of entrapped $CuCl_2$ crystallites can be estimated from the area under the main peak of $CuCl_2$ diffraction patterns at $2\theta = 17.2°$. These values demonstrate that in the case of 10% and 16% all $CuCl_2$ is bonded to the matrix whereas at higher concentrations the introduced $CuCl_2$ is present in

TABLE 1 Selected XRD Data for the PDMSEN-$CuCl_2$ Macromolecules-Containing Varying Amounts of $CuCl_2$

% $CuCl_2$ introduced in PDMSEN matrix	$2\theta(^\circ)^a$	d(Å)	% $CuCl_2$ fine crystallites physically entrapped in the PDMSEN matrix^d	% $CuCl_2$ chemically attached to the PDMSEN matrix^e
PDMSEN	14.95	6.880	^{b}	—
10	10.90	8.107	^{b}	10
16	10.88	8.122	^{b}	16
20	10.69	8.266	5.4	14.6
26	10.91	8.100	8.9	17.1
30	10.95	8.074	^{c}	^{c}
40	10.98	8.048	15.8	24.2
50	11.03	8.011	24.6	25.4

$^a2\theta$ values of the main broad peak due to PDMSEN matrix. ^{b}Pure $CuCl_2$ crystallite lattices are not detected. ^{c}Very broad. ^{d}The % of $CuCl_2$ crystallite entrapped into the PDMSEN-$CuCl_2$ macromolecules normalized to the main sharp peak of $CuCl_2$. ^{e}The amounts of $CuCl_2$ chemically attached to the PDMSEN matrix can be calculated from the difference between columns 1 and 4.

two forms, chemically bonded to the PDMSEN matrix and physically entrapped into the matrix as shown in Table 1. Moreover, as the amounts of pure $CuCl_2$ increase beyond 26%, the inter-chain spacing remained almost constant, Figure 4, suggesting that $CuCl_2$ crystallites grow uniaxially with PDMSEN chain direction, thus causing no further inter-chain space expansion.

The dependence of relative permittivity (ε') on frequency is shown in Figure 5a, where the ε' is minimum for samples that contain high contents of $CuCl_2$. The sharp increase in dielectric permittivity (ε') at low frequency and dielectric loss (ε'') as shown in Figure 5b are mainly due to ionic conduction. However no relaxation peak was observed in the plot of the loss factor (ε'') shown in Figure 5b. It is believed that the ion conduction may mask any relaxation. Therefore, to analyze the conductivity relaxation process, the complex permittivity ε^* is converted to the complex electric modulus M^* according to the following relations (Macedo et al.) [20].

$$M' = \varepsilon'/\varepsilon'^2 + \varepsilon''^2$$

$$M'' = \varepsilon''/\varepsilon'^2 + \varepsilon''^2$$

In these relations, ε' appears as in the denominator to the second power, and its tendency to overwhelm the loss factor is minimized. In addition, the electric modulus can explain the dispersion of ε^* with

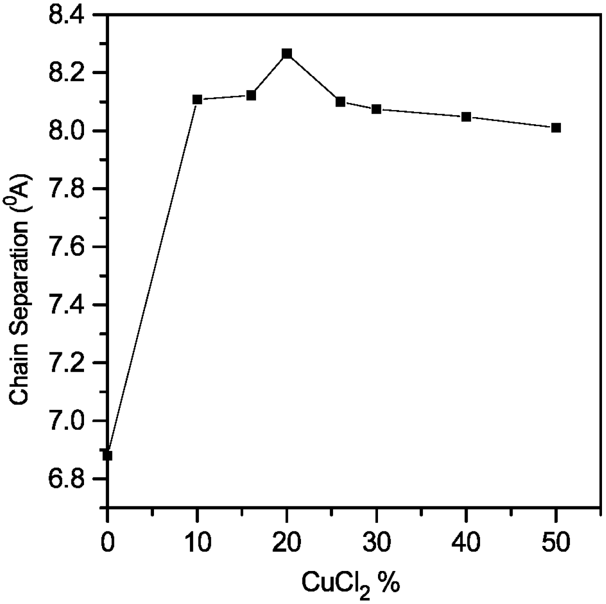


FIGURE 4 A plot of PDMSEN chain-chain separation as a function of $CuCl_2$%.

frequency without any molecular polarization phenomena. From the dependence of M′ and M″ on frequency as shown in Figures 6a and 6b, the dispersion of M′ and M″ indicates the presence of the relaxation time distribution of conduction. M′ in Figure 6a for samples containing 5% to 16% of $CuCl_2$ approaches zero at low frequencies indicating that electrode polarization gives a negligible low contribution to M′ and can be ignored. The peak maxima of the M″ for $CuCl_2$ contents decrease in intensity and move toward higher frequencies. This coincides well with the results of Lee et al. [21] who found that in doped polymers, the peak shifts toward higher frequencies with increasing dc conductivity. However, Broad peaks where observed for all samples that may involve two relaxation processes. This is clear in the sample that contains 5% of $CuCl_2$, where two relaxation processes can be detected. This is clearly demonstrated in the plot of M′ versus M″, where two semi-circles were observed in the low content of $CuCl_2$, as shown in Figure 6c.

Concerning the dielectric permittivity, Hourquebie and Olemo [22] suggested the following formula for the dependence of ε'' on frequency

$$\varepsilon''(f) \propto f^{-n}$$

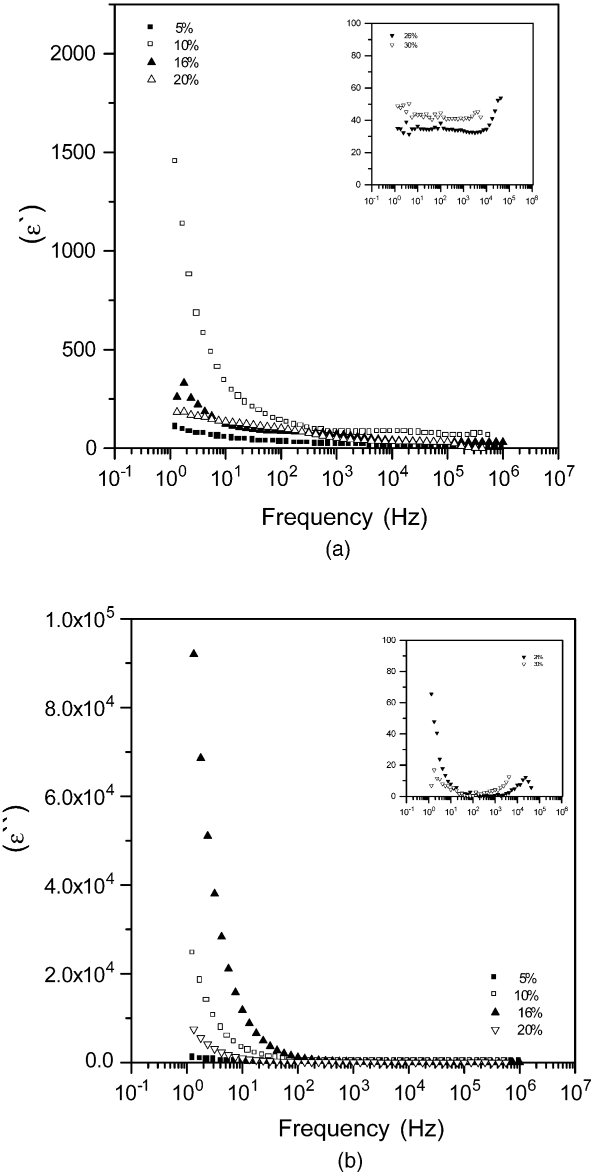
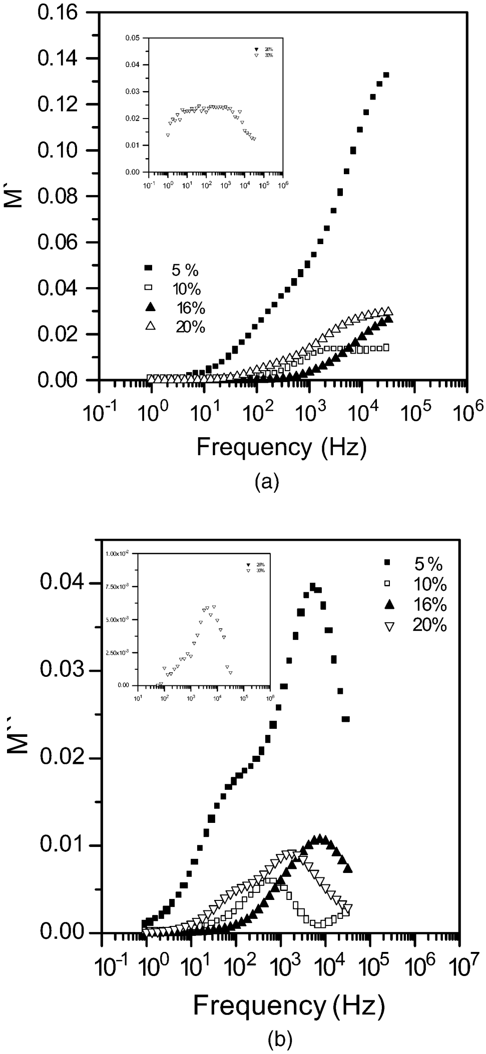


FIGURE 5 (a) Dielectric permttivity (ε') versus frequency for polycarbosilazane-based $CuCl_2$. (b) Dielectric loss (ε'') versus frequency for polycarbosilazane-based $CuCl_2$.



(a)

(b)

FIGURE 6 (a) Real (M′) component of electric modulus versus frequency for polycarbosilazane-based $CuCl_2$. (b) Imaginary compnent (M″) versus frequency for polycarbosilazane-based $CuCl_2$. (c) Real (M′) versus imaginary component (M″) of electric modulus for polycarbosilazane-based $CuCl_2$.

Figure 7 shows the plot of log ε'' versus frequency for the samples that contain up to 16% $CuCl_2$. The experimental curves in the frequency range 200 Hz to 10^4 Hz, show good linearity, Therefore this formula is convenient to calculate ε'' for this frequency range. Calculated (n)

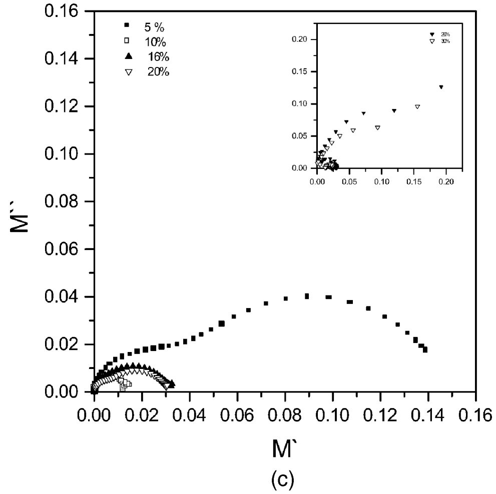


FIGURE 6 Continued.

for the samples that contain 5%, 10%, and 16% $CuCl_2$ give the values of (n) as 0.87, 0.95, 0.96, respectively. Thus the conductivity would be nearly $\sigma \propto f^{-0.94}$ indicating that the conductivity should increase with

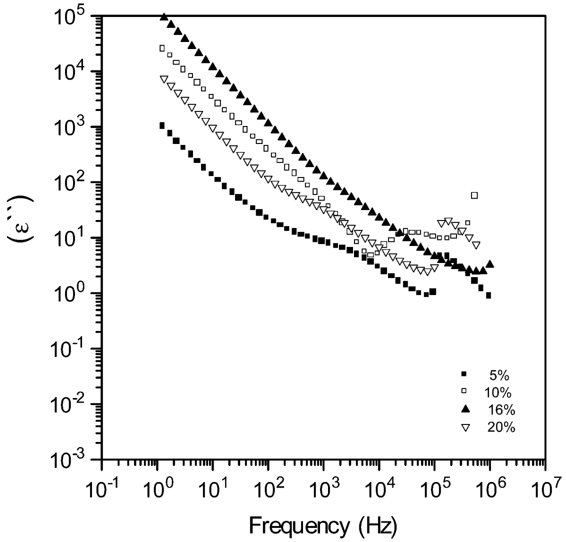


FIGURE 7 Log dielectric loss (ε'') versus frequency for polycarbosilazane-based $CuCl_2$.

decreasing frequency. Therefore, the conduction mechanism in this system is by means of jumping (carrier hopping). The increase in the concentration up to 16% makes hopping between the chains easier, and thus results in an increase of conductivity. When the concentration exceeds 20%, $CuCl_2$ starts to form clusters that lead to an increase in the interaction distances, which makes hopping between chains more difficult, and thus causing a reduction of conductivity.

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