

Dielectric Relaxation and Alternating-Current Conductivity of Gadolinium-Doped Poly(vinyl alcohol)

T. A. Hanafy

Physics Department, Faculty of Science, Fayoum University, Fayoum 63514, Egypt

Received 6 May 2007; accepted 19 September 2007

DOI 10.1002/app.27567

Published online 20 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The dielectric constant, dielectric loss factor, and alternating-current conductivity of Gd-doped poly(vinyl alcohol) (PVA) samples have been studied in the temperature and frequency ranges of 290–450 K and $50\text{--}5 \times 10^6$ Hz, respectively. Three relaxation processes— α_a , α_c , and ρ —have been obtained. The first one is due to the rotation of OH and C=O groups inside the amorphous part of PVA. The second process is due to the dipole relaxation in the crystalline phase of the sample. The changes in the peak position and height of α_a and α_c have been interpreted in light of the formation of complexes between GdCl₃ and OH and C=O groups of the PVA structure. On the other hand, the ρ -relaxation process is due to the space-charge formation between the different phases

inside the PVA samples. Alternating-current conductivity measurements of the investigated samples have revealed that the hopping conduction mechanism is predominant. The maximum barrier height and the activation energy have been calculated and reported. In the low temperature range (306–333 K), the responsible conduction mechanisms of PVA doped with 2 or 4 wt % GdCl₃ have been found to be small polaron tunneling and quantum mechanical tunneling, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2540–2549, 2008

Key words: charge transfer; dielectric properties; metal-polymer complexes

INTRODUCTION

The incorporation of metal salts into polar organic polymers can induce pronounced changes in various properties of the polymers.^{1–3} Frequency shifts and intensity changes in the infrared vibrations of polyamide (nylon 6) containing added metal halides⁴ and the changes in the spectra of several polymers doped with inorganic nitrates⁵ have been interpreted in terms of complex formation between the metal salts and specific functional groups of the polymers. The incorporation of metal chlorides (CoCl₂, CuCl₂, and FeCl₃) into poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA) produced intensity changes in infrared absorption bands of the polymers and resulted in a 10^6 -fold increase in the electrical conductivity of the films.^{6–8}

These effects resulted in a new, specific metal-polymer interaction, for which a model based on strong electrical coupling between the metal atoms and polar C—Cl and C—OH bonds of PVC and PVA, respectively, was presented.^{7,8} Recently, it was reported that the incorporation of rare-earth salts and their complexes into solution-grown thin polymer films produced a metastable state lifetime, which should be maximized for laser properties, giving rise

to very strong luminescence.^{9–12} Rare-earth cations are often characterized by a reduced affinity to complex formation in comparison with trivalent cations of other metals (Fe³⁺, Cr³⁺, Al³⁺, etc.). This is due to the relatively large size of the rare-earth cations, weak electrostatic interactions between such cations and negatively charged ligands, and the low capacity for covalent-bond formation. This results from the features of the electronic structure of lanthanides.^{13,14} As a result, rare-earth cations form complexes with bonds of a mainly ionic (electrostatic) nature.^{13,14}

Rare-earth complexes such as europium and samarium are suitable candidates for applications such as light-emitting diodes, optical fibers, laser materials, and optical signal amplifications.^{13–15} Moreover, rare-earth salts have a considerable effect on the structure and optical and electrical properties of polymers.^{7–12}

The aim of this work was to investigate the effect of the Gd cation concentration on the dielectric constant (ϵ') values and alternating-current (ac) conduction mechanisms of PVA to improve the properties of PVA to make it more applicable.

EXPERIMENTAL

PVA, obtained from Avondale Laboratories (Banbury Oxon, England), had an average molecular weight of 17,000 GRG. Gadolinium chloride hydrate

Correspondence to: T. A. Hanafy (tahanafy2@yahoo.com).

(GdCl_3 ; 99.99%) was obtained from Sigma–Aldrich (Steinheim, Germany). PVA powder was dissolved in triply distilled water at 80°C with continuous stirring. The mixture was kept at 80°C for 30 min until a clear solution was obtained. The solution was cooled slowly with continuous stirring at 50°C . GdCl_3 was dissolved in 0.5–1 mL of concentrated HCl, and the mixture was diluted by the addition of 10 mL of triply distilled water at 50°C with continuous stirring. The mixture was added to the PVA solution at 50°C with continuous stirring of the final mixture for 12 h.

The aqueous solution of the mixture was cast into a Petri dish placed on a leveled plate at room temperature (35°C) for 7 days until the solvent was completely evaporated. The obtained polymer film, 0.08 mm thick, was cut into square pieces and coated with silver paste to achieve ohmic contacts. The ϵ' measurements were carried out with a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR, the accuracy of which for measuring the capacitance was of the order of 0.0001 pF.

The temperature was measured with a T-type thermocouple with its junctions just in contact with the sample with accuracy better than $\pm 1^\circ\text{C}$. PVA films filled with mass fraction (W) values of 0, 2, 4, 6, and 8 wt % GdCl_3 were prepared. W was calculated as follows:

$$W(\text{wt } \%) = w_f / (w_p + w_f) \times 100 \quad (1)$$

where w_f and w_p represent the weights of the filler and polymer, respectively.

RESULTS AND DISCUSSION

The temperature dependence of ϵ' and the dielectric loss factor (ϵ'') of pure PVA, in the frequency range of 10 kHz to 1 MHz, is shown in Figure 1(a,b), respectively. The figure shows the existence of two relaxation peaks, designated α_a and α_c , at 336 and 383 K for $\epsilon'(T)$ and at 330 and 373 K for $\epsilon''(T)$, respectively. The sharp α_a peak centered at 330 K for $\epsilon''(T)$ is accompanied by a sharp peak for $\epsilon'(T)$ at 333 K. This process corresponds to the segmental relaxation associated with the glass transition, at which the micro-Brownian motion of long chain segments in the amorphous regions of PVA takes place.

Moreover, the α_c peak, which is located at 370 K for $\epsilon''(T)$ and at 383 K for $\epsilon'(T)$, is related to the segmental motion in the crystalline phase of PVA.¹⁶ This process is probably due to the dipole relaxation in the crystalline phase or in the region intermediate between the amorphous and crystalline phases of the PVA structure. Also, the high-temperature α_c is broad and therefore involves a distributed polarization.

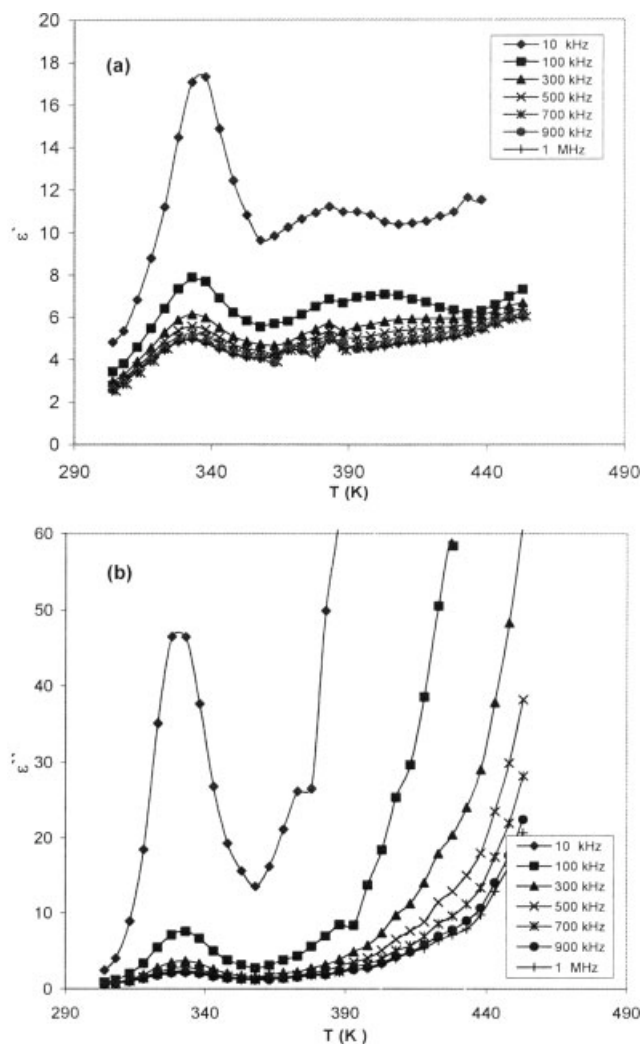


Figure 1 Temperature (T) dependence of (a) ϵ' and (b) ϵ'' for pure PVA at constant frequencies.

Figure 2(a–d) shows the temperature dependence of ϵ' for PVA doped with 2, 4, 6, or 8 wt % GdCl_3 in the frequency range of 10 kHz to 1 MHz, respectively. From the figure, it can be seen that $\epsilon'(T)$ exhibits the same trend as $\epsilon'(T)$ for pure PVA. At 10 kHz, the peak position of α_a of PVA doped with 2 wt % GdCl_3 has shifted to a higher temperature at 340 K, whereas the broad α_c peak has become more intense, and its peak position has shifted to a lower temperature at 360 K. In addition, the peak height of α_a and α_c has increased to 107 and 93, respectively.

When the Gd concentration increases to 4 wt % inside the backbone structure of PVA, the α_c -relaxation process completely vanishes. Also, the peak position of α_a indicates that the glass-transition temperature (T_g) of PVA has shifted to a higher temperature at 347 K, and its peak height has become 71. Figure 2(c,d) shows that the introduction of GdCl_3 at 6 wt % within a PVA film increases the values of ϵ' and shifts T_g of the polymer toward lower values at

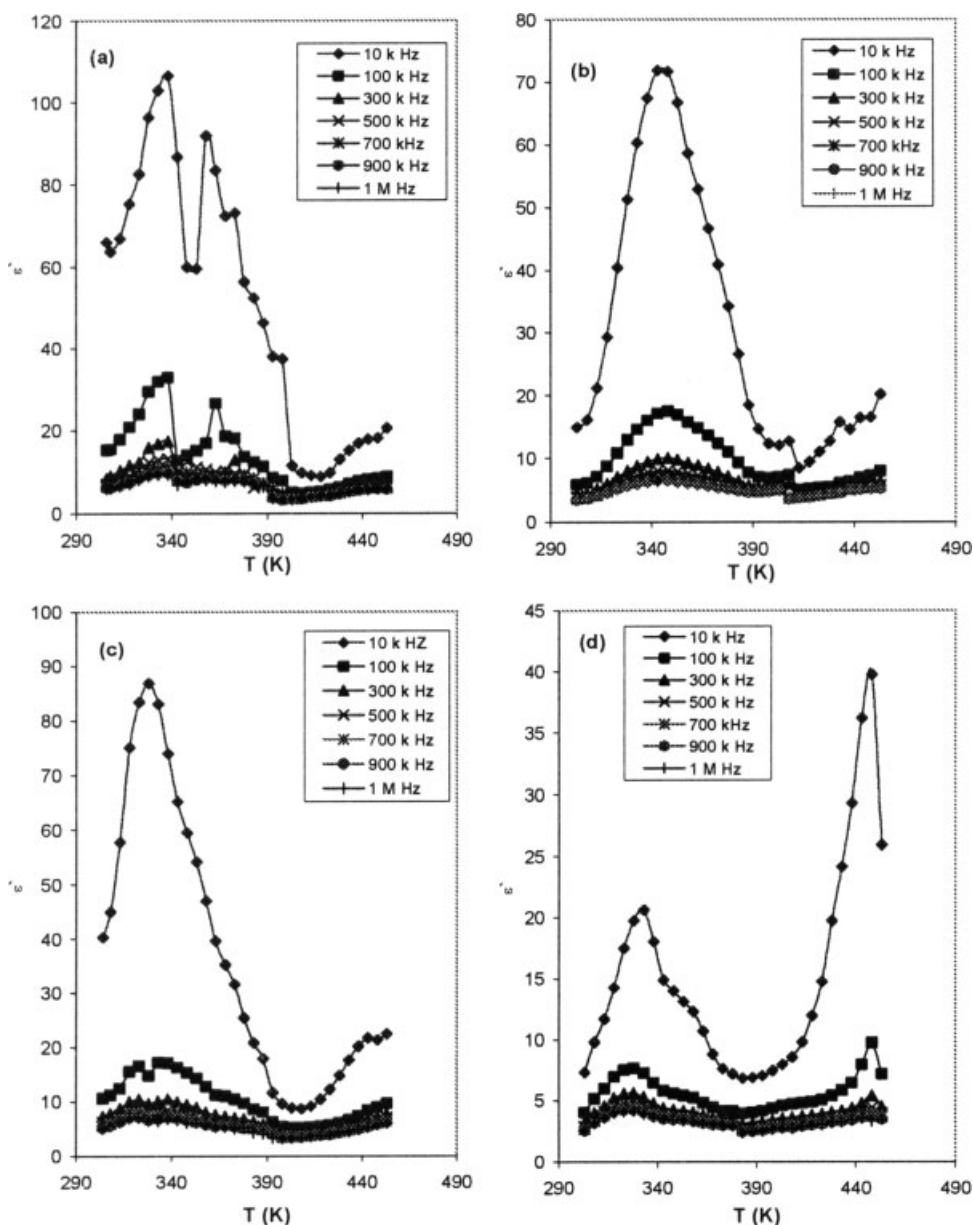


Figure 2 Temperature (T) dependence of ϵ' for PVA doped with (a) 2, (b) 4, (c) 6, or (d) 8 wt % GdCl_3 at constant frequencies.

330 K. Moreover, PVA that contains 8 wt % GdCl_3 undergoes a decrease in the peak height of α_a at 20.5, and its peak position shifts to a lower temperature at 333 K.

There are several factors¹⁷ that influence T_g for polymers, such as main-chain rigidity, crosslinking density, and the chemical structure of the dopant materials. The PVA hydroxyl groups contribute, by hydrogen bonding, to the stiffness of the linear polymer. By the introduction of lanthanides as crosslinking agents, the number of hydroxyl groups may diminish, and hydrogen-bonding interaction decreases; this produces a diminution in the stiffness. This can be ascribed to the higher coordination number of lanthanides, such as Gd. Also, there are many possibil-

ities for the formation of varieties of topologies inside the polymers.^{18–20} On the other hand, crosslinking increases the rigidity, and the new moieties that are produced can affect T_g in different ways, depending on crosslinking formation inside the amorphous and crystalline regions inside the PVA structure.

The trend of T_{α_a} (peak position of α -relaxation due to the amorphous parts of the PVA samples), corresponding to T_g , for PVA samples as a function of the Gd concentration is shown in Figure 3. The increase in the Gd content within the PVA sample from 2 to 4 wt % increases T_g of the sample from 333 to 347 K. This may be due to the formation of complexes between Gd^{3+} and hydroxyl (OH) and carbonyl (C=O) groups of the main chain. More-

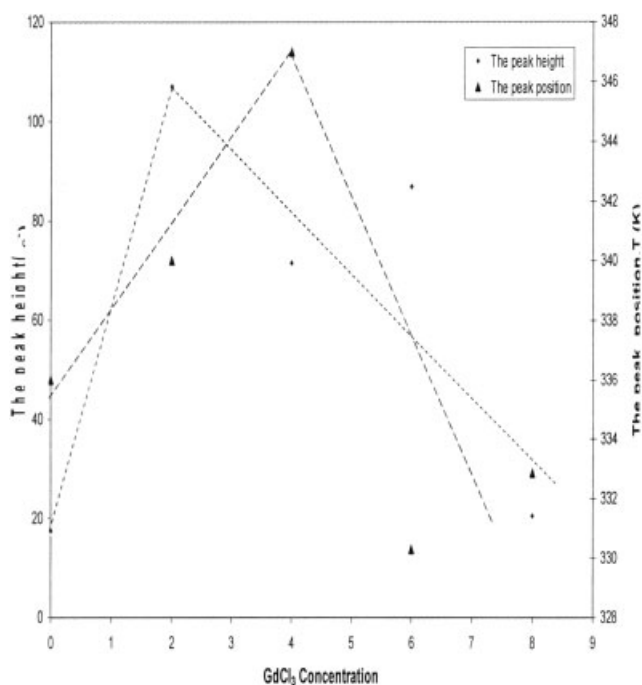


Figure 3 Peak position and peak height of the α_c -relaxation process for pure PVA and doped samples.

over, hydrogen-bonding formation may play an important role in this process. As a result, Gd^{3+} ions can form metal-ligand complexes within the PVA structure. These complexes can be bound via coordination and ionic bonds with OH groups of the next layer of polyanion molecules accompanying the completion of metal complexes and creation of a new film substrate. In this approach, multivalent Gd^{3+} ions act intrinsically as structure-forming linking components for the resulting material, and the multiple salt bridges and coordination bonds result in the formation of a condensed structure.

Consequently, Gd-PVA crosslinking within the amorphous regions acts as a PVA stabilizer that increases T_g of PVA. However, the crosslinking formation in the crystalline regions acts as a PVA plasticizer, with respect to $T\alpha_c$ (peak position of α -relaxation due to the crystalline parts of the PVA samples), leading to wide spacing between polymer chains; as a result, the disorder degree and the free volume are increased in this region. Therefore, the formation of Gd-PVA complexes increases the free volume²¹ in the crystalline regions and lowers $T\alpha_c$. Growth in the free volume also lowers the interaction between molecules. In addition, the crosslinking formation may screen the polar groups of PVA and prevent the formation of polymer-polymer bonds, lowering $T\alpha_c$. Then, a more ordered arrangement of the polymer chains is obtained, which increases the polarization and ϵ' of the sample.

Figure 4(a,b) presents the temperature dependence of ϵ' and ϵ'' of pure and doped PVA samples, respectively, at 10 kHz. All the doped samples exhibit

another relaxation process ρ peak around 445 K. The peak height of this process was found to increase with the Gd^{3+} concentration. This process may be assigned to the formation of more than one phase inside the PVA structure via the formation of Gd-PVA complexes. The nature of the ρ -relaxation process for semicrystalline polymers is due to chain trapping of interfaces or Maxwell-Wagner polarization phenomena within the samples.²²

However, in the amorphous parts of the investigated sample, the ρ process is related to conductive impurities, injected space charges, and electrode effects. The ρ peak clearly originates from the motion of space charges, which have accumulated in the polymer close to the electrodes. Therefore, this process depends on the nature of the electrode and the presence of impurities such as water molecules.²³ Moreover, the ρ peak is always appearing above the dipolar α peak; the latter arises from the displacement of charges, whereas the former arises from the gross motion of charges over macroscopic distances.

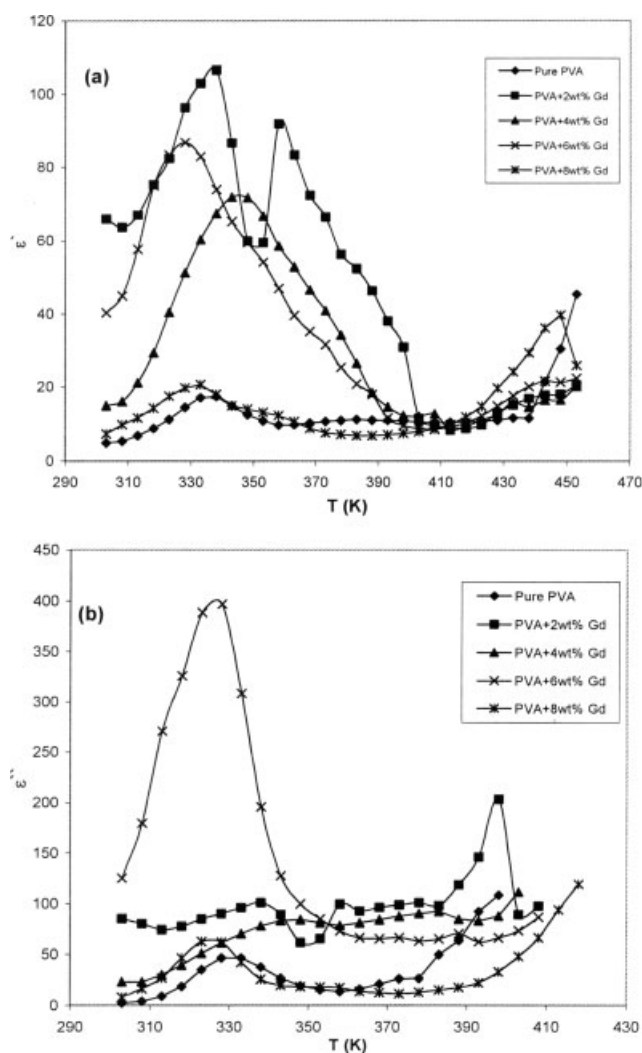


Figure 4 Temperature (T) dependence of (a) ϵ' and (b) ϵ'' for the investigated samples at 10 kHz.

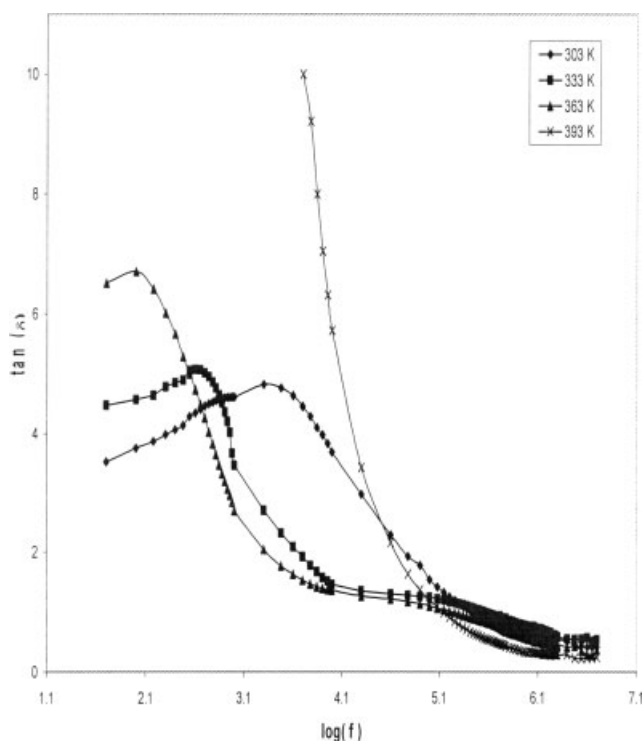


Figure 5 Frequency (f) dependence of $\tan \delta$ of PVA doped with 4 wt % GdCl_3 at constant temperatures.

Figure 5 shows the dielectric loss ($\tan \delta$) of PVA doped with 4 wt % GdCl_3 as a function of frequency at 303, 333, 363, and 393 K. In the isothermal frequency scans of $\tan \delta$, the two relaxation processes, called ρ and α , are detected around 200 Hz to 3 kHz and 100 kHz to 3 MHz, respectively. The α -loss peak is shifted to higher frequencies with the temperature increasing from 303 to 393 K. The peak broadening of this process may be assigned to the diminution of the crystallinity of the system, which is caused by the increase in the crosslinking density.^{24,25} However, there is a competitive action of at least three factors during the crosslinking:

1. Diminution of the existing physical network due to the hydrogen bonding.
2. Formation of a chemical network.
3. Crosslinking formation inside the amorphous regions.

The ρ -loss peak is shifted to a lower frequency with increasing temperature; this may be attributed to the space charge in the interface between the oriented regions. On the other hand, this transition in the Gd-PVA structure may be related to multiphases coming from the conformation of the structure of complexes between Gd^{3+} and OH and C=O groups of the PVA main chain. In addition, the interactions of a number of rare-earth metal cations (Gd^{3+} , Nd^{3+} , Er^{3+} , etc.) with other polymers have been studied,

and the formation of complexes between the metal cations and the ligand groups of the polymers has been investigated.^{1-3,14}

Figure 6(a-c) illustrates the frequency dependence of $\tan \delta$ for a pure PVA sample and samples containing 2, 4, 6, or 8 wt % GdCl_3 at constant temperatures of 303, 333, and 363 K, respectively. The data show that all PVA samples undergo two relaxation processes (α and ρ), except for pure PVA at 363 K, which exhibits α relaxation only. The maximum broadening and peak position (2 kHz at 303 K) for the ρ peak were obtained for PVA doped with 4 wt % GdCl_3 . The height of the α peak was found to increase with the Gd salt content from 2 to 4 wt % and then decrease with a further increase of Gd salt in the sample. This may be due to the competitive rotation of OH and C=O groups of the main chains. In addition, the plasticization effect of the Gd-PVA crosslinking plays a significant role in increasing the free volume between the PVA main chains. This leads to an increase in both $\tan \delta$ and ϵ' . The higher the GdCl_3 concentration (6 and 8 wt %) is, the higher the crosslinking density is; this screens the polar groups of the polymer and decreases the peak height of the α -relaxation process.

The increment of T_g is probably a result of the PVA- GdCl_3 interaction and high crosslinking density, which restrict the polymer chain mobility. This leads to the formation of an immobilized polymer shell around Gd^{3+} ions,¹³ and thereat, the rigidity of chains increases within the polymer matrix, as confirmed by the mechanical properties.^{26,27} It has been found that chemical crosslinking of a linear polymer, such as PVA, may provide feasible routes for improvement of the mechanical properties and thermal stability.^{28,29} Several crosslinking methods have been published for different uses and applications.^{30,31} Crosslinking PVA has found a very promising application in the preparation of biomedical materials³² and magnetic-field-sensitive gels.³³ Furthermore, lanthanide metals such as Gd(III) have higher sensitivities for magnetic resonance imaging examinations.¹³

Figure 7(a,b) shows the measured ac conductivity as a function of the reciprocal temperature [$\sigma(T)$] at different frequencies for pure PVA and PVA containing 2, 4, 6, or 8 wt % GdCl_3 at 100 kHz, respectively. This figure reveals that the $\sigma(T)$ values of all the samples exhibit two regions at low and high temperatures (I and II, respectively). These regions obey the Arrhenius equation:

$$\sigma(T) = \sigma_0 \exp(-E_a/kT) \quad (2)$$

where σ_0 is a constant, k is Boltzmann's constant, E_a is the activation energy, and T is the absolute temperature. The E_a values were calculated for all samples

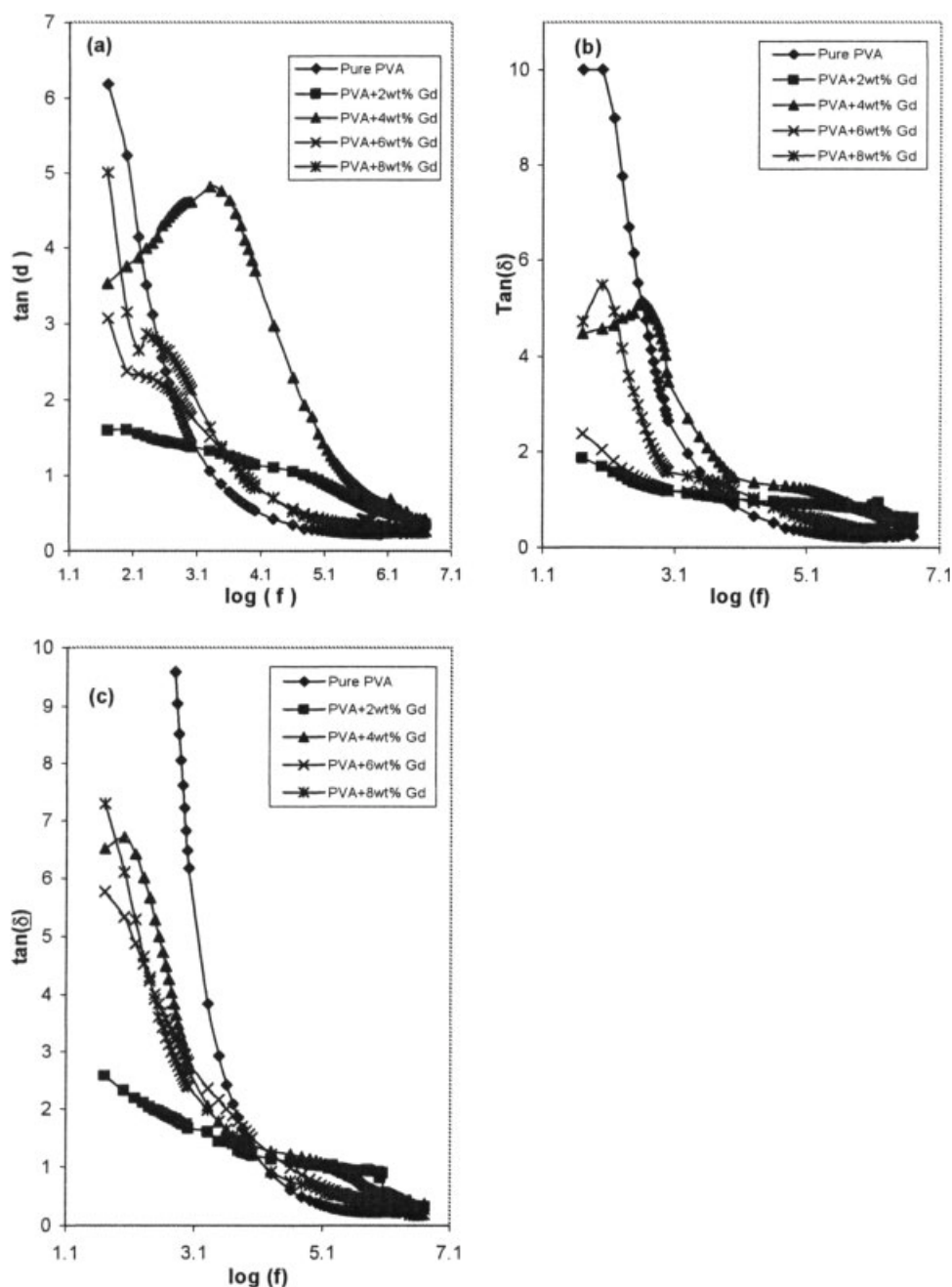


Figure 6 Frequency (f) dependence of $\tan \delta$ of pure PVA and doped samples at (a) 303, (b) 333, and (c) 363 K.

at 100 kHz and are reported in Table I. The ac conductivity (σ_{ac}) of pure PVA was found to increase with the ambient temperature and field frequency increasing. This reveals that the mechanism responsible for the conduction mechanism could be a hopping one.⁷ Also, the variation of the conductance with temperature is due to a combined effect of a change in the conductance with temperature and the nature of trap distribution in the sample. This indicates that the conductance takes place via hopping of carriers between randomly distributed trapping centers in amorphous and crystalline regions. The

increase in the values of $\sigma(T)$ at higher temperatures suggests that the variable range of hopping conduction mechanisms of charge carriers is operative.

Moreover, σ_{ac} of the PVA samples increased with the Gd content. This result can be investigated by consideration of the following three effects:

1. The Gd ion has an ionic radius of 1.02 \AA ,³⁴ so the average metallic particle to particle separation decreases as the Gd^{3+} content increases. This tends to increase the electrostatic fields between Gd^{3+} ions.

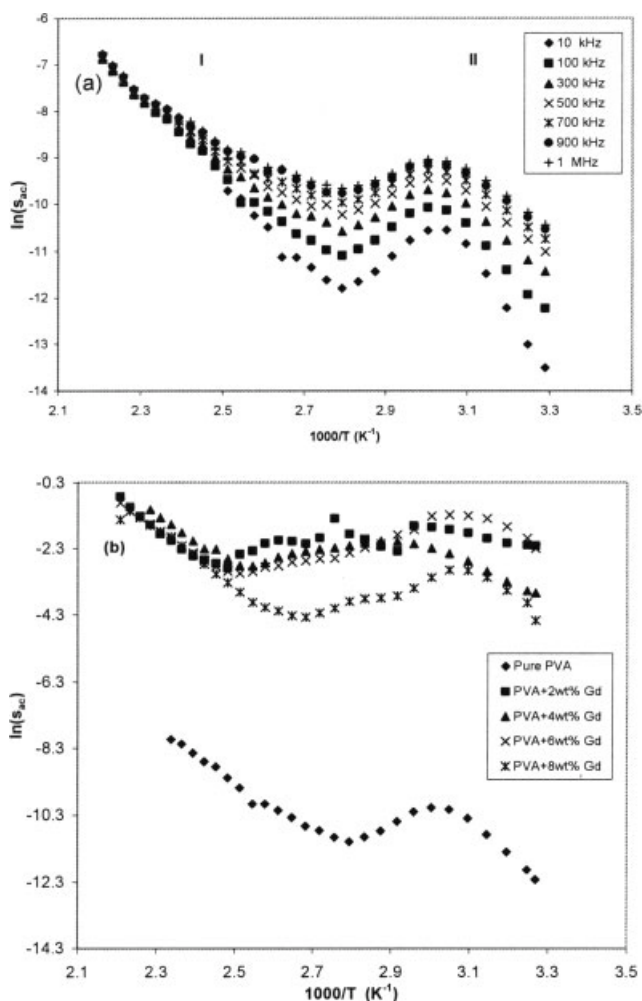


Figure 7 Relation between σ_{ac} and $1000/T$ of pure PVA and doped samples at 100 kHz.

- The formation of Gd-PVA complexes may increase the nature of the trap centers and lower the potential barrier to detrapping.³⁵ The traps may be a result of disorder, contributing to the observed hopping conduction mechanism.
- Transition metals may reside at the amorphous-crystalline boundaries and diffuse preferentially, via heating, through the amorphous

regions and thus form a charge transfer with the polymeric chains.³⁶

The behavior of the ac conductivity as a function of frequency ω [$\sigma_{ac}(\omega)$] for the amorphous semiconductors is given by³⁷

$$\sigma_{ac}(\omega) = A\omega^S \quad (3)$$

where A is constant and exponent S is a function of ω . Several theoretical models have been proposed to interpret the ac conduction mechanism for amorphous semiconductors. It is assumed that the dielectric loss occurs because of the localized motion of the charge carriers within a pair of sites. Two distinct mechanisms have been proposed for relaxation phenomena: quantum mechanical tunneling (QMT) of electrons or polarons through the barrier separating localized states and classical hopping over the same barrier.

Small polaron tunneling (SPT) may be formed in a covalent solid if the addition of a charge carrier to a site causes a large degree of local lattice distortion. In this case, the activation energy for polaron transfer or the maximum barrier height, $W_H \approx 1/2W_p$ (where W_p is the polaron energy), is independent of the intersite separation, and the temperature dependence of S should follow this equation:³⁷

$$S = 1 - 4[\ln(1/\omega\tau) - W_H/kT]^{-1} \quad (4)$$

where τ is the characteristic relaxation time. For QMT, it is assumed that there is no lattice distortion associated with the carrier movements and that S is temperature-independent. Frequency exponent S in this model is reduced to

$$S = 1 - 4[\ln(1/\omega\tau)]^{-1} \quad (5)$$

This indicates that S values are temperature-independent.

The correlated barrier hopping (CBH) model was first proposed by Picke³⁸ to account for ac conduction in amorphous scandium oxide films. It is assumed that single electron motion is responsible, and then $\sigma_{ac}(\omega)$ in this model is expressed by

TABLE I
Values of E_a and W_H Corresponding to the CBH Model for All the PVA Samples

Sample	E_a (eV)		W_H (eV)	
	I	II	In the α_a -relaxation process	In the ρ -relaxation process
Pure PVA	0.83	0.78	0.54	0.35
PVA + 2 wt % GdCl ₃	0.20	0.69		0.31
PVA + 4 wt % GdCl ₃	0.51	0.74		0.30
PVA + 6 wt % GdCl ₃	0.54	0.65	0.35	0.31
PVA + 8 wt % GdCl ₃	0.61	0.76	0.42	0.32

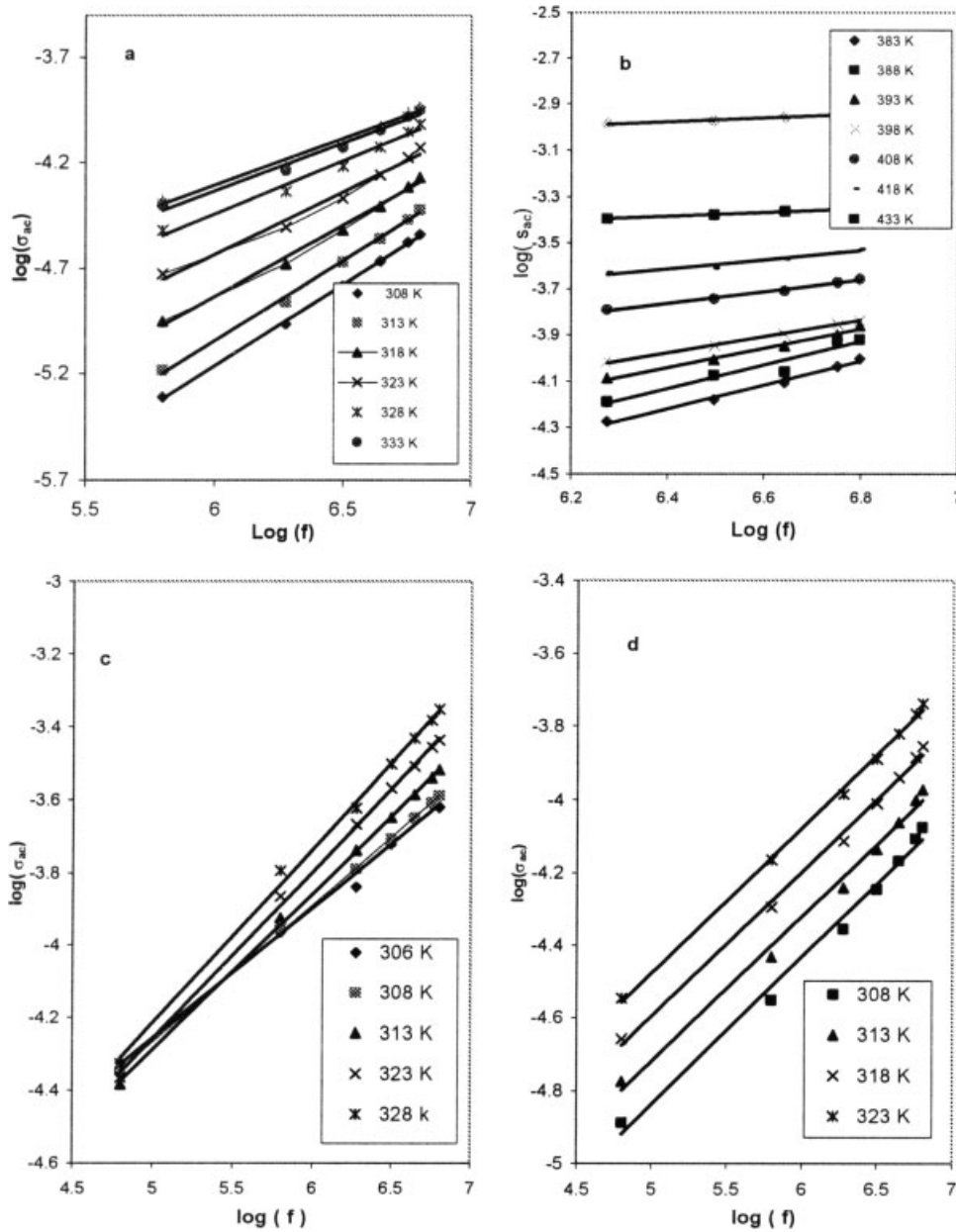


Figure 8 Relation between $\log \sigma_{ac}$ and the logarithm of the frequency ($\log f$): (a) pure PVA in the α_a -relaxation process, (b) pure PVA in the ρ -relaxation process, (c) PVA doped with 2 wt % GdCl_3 in the α_a -relaxation process, and (d) PVA doped with 4 wt % GdCl_3 in the α_a -relaxation process.

$$\sigma_{ac}(\omega) = \pi^3/24[N^2\epsilon'\epsilon_0\omega R_\omega^6] \tag{6}$$

where ϵ_0 is the dielectric permittivity of the free space and N is the density of a pair of sites. The hopping length (R_ω) is given by

$$R_\omega = e^2/\pi\epsilon'\epsilon_0[W_H - kT \ln(1/\omega\tau)]^{-1} \tag{7}$$

where e is the electronic charge. Frequency exponent S in the electron CBH model is evaluated as follows:

$$S = 1 - 6kT[W_H - kT \ln(1/(\omega\tau))]^{-1} \tag{8}$$

For large values of W_H/kT , S becomes³⁹

$$S = 1 - 6kT/W_H \tag{9}$$

To specify the dominant ac conduction mechanism for all PVA samples, the frequency dependence of σ_{ac} at a constant temperature corresponding to the lower temperature side of both α_a - and ρ -relaxation processes has been considered. The $\log \sigma_{ac}$ - $\log \omega$ plots of pure PVA for α_a at 308–333 K and for ρ at 383–418 K are shown in Figure 8(a,b), respectively. Also, the frequency dependence of σ_{ac} for PVA doped with 2 or 4 wt % GdCl_3 for the α_a -relaxation

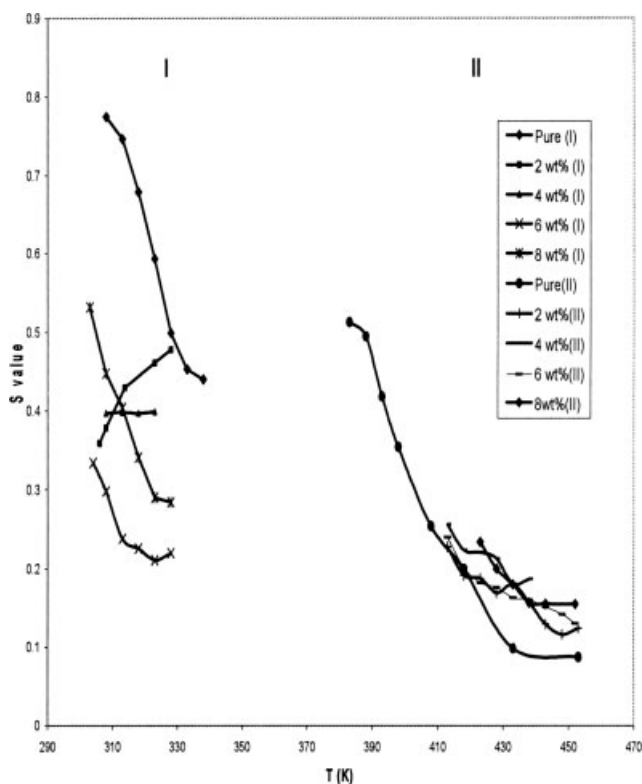


Figure 9 Variation of exponent S with the temperature (T) for all PVA samples in the α_a -relaxation (region I) and ρ -relaxation (region II) processes.

process at 306–328 K is shown in Figure 8(c,d), respectively. The measured data show that σ_{ac} increases linearly for all PVA samples with the field frequency.

The temperature dependence of exponent S for all PVA samples for the α_a -relaxation and ρ -relaxation processes is shown in Figure 9. It is evident from this figure that the S values decreased with increasing temperature for PVA for both α_a -relaxation and ρ -relaxation processes. This suggests that the variation follows eq. (9), indicating the predominance of the CBH mechanism. The calculated values of W_H are listed in Table I. These values are nearly equal to half the values calculated for E_a of the samples. This may be attributed to the existence of the microinhomogeneity of the investigated samples.

The increase in S values with increasing temperature for PVA doped with 2 wt % GdCl_3 indicates that the conduction mechanism could be an SPT one.²⁹ This may be due to the local lattice distortion, which resulted from Gd–PVA crosslinking formation. Therefore, the total energy (electron + distortion) of the system is lowered by W_p .²⁹ This may be responsible for the existence of the higher values of σ_{ac} of this sample in comparison with other PVA samples.

In addition, the behavior of S components for PVA doped with 4 wt % GdCl_3 is temperature-inde-

pendent. This reveals that a QMT mechanism is predominant in this system. Thus, with increasing Gd content inside the PVA structure, the Gd–PVA cross-linking density increases. Overlap on the cloud charges, which results from the large degree of local lattice distortion, is obtained. Therefore, the uniform distribution of these clouds may be attained within the PVA structure, and the conduction mechanism could be a QMT one.

It can be expected that higher complex formation density inside the PVA structure will be obtained with 6 and 8 wt % GdCl_3 as the doping materials. This leads to the formation of multiple domains or phases within the investigated samples. Thus, the electron transfer by thermal activation over the barrier between two sites may be suggested to be the related conduction mechanism in these systems. In addition, the values of exponent S in α_a - and ρ -relaxation processes have been found to decrease with increasing temperature, as shown in Figure 9. This indicates that the conduction mechanism of PVA doped with 6 or 8 wt % GdCl_3 is CBH.

CONCLUSIONS

The temperature and frequency dependence of ϵ' allows us to detect three relaxation transitions in PVA samples. The first one occurs at T_g (α_a), and the second (α_c), which is attributed to the dipole relaxation inside the crystalline regions, is located near 388 K for pure PVA. The third one is the space-charge transition (ρ), which is due to the chain trapping of the interfaces or the Maxwell–Wagner polarization within the sample. The disappearance of the α_c -relaxation peak for PVA doped with 6 or 8 wt % GdCl_3 is attributed to the formation of complexes and the distortion process within the crystalline phase of the PVA structure. σ_{ac} of the investigated samples reveals that CBH is the most probable conduction mechanism at lower and higher temperature regions. However, at 306–333 K, the conduction mechanisms of PVA samples doped with 2 and 4 wt % GdCl_3 could be SPT and QMT, respectively.

References

- de Oliveira, H. P.; dos Santos, M. V. B.; dos Santos, C. G.; de Melo, C. P. *Mater Char* 2003, 50, 223.
- Ahmed, M. A.; Basha, A. M.; Marey, H. K.; Hanafy, T. A. *J Appl Polym Sci* 2001, 79, 1749.
- Zheng, Z.; Liang, H.; Ming, H.; Zhang, Q.; Xie, J. *J Opt Commun* 2004, 233, 149.
- Dunn, P.; Sanson, G. F. *J Appl Polym Sci* 1969, 13, 1641.
- Wissbrun, K. F.; Hannon, M. J. *J Polym Sci Part B: Polym Phys* 1975, 13, 223.
- Rao, T. V.; Chopra, K. L. *Thin Solid Films* 1979, 60, 387.
- El Kader, F. H.; Attia, G.; Ibrahim, S. S. *Polym Degrad Stab* 1994, 43, 253.
- Tawansi, A.; El Kodary, A.; Abdelnaby, M. M. *Curr Appl Phys* 2005, 5, 572.

9. Xie, F.; Zheng, Z. *Phys B* 2004, 349, 415.
10. Suzuki, H.; Hattori, Y.; Iizuka, T.; Yuzawa, K.; Matsumoto, N. *Thin Solid Films* 2003, 438, 288.
11. Huang, H.; Yan, B. *Mater Sci Eng B* 2005, 117, 261.
12. Kumar, G. A. *Mater Lett* 2002, 55, 364.
13. Takahashi, M.; Hara, Y.; Aoshima, K.; Kurihara, H.; Oshikawa, T.; Yamashita, M. *Tetrahedron Lett* 2000, 41, 8485.
14. Khomutov, G. B.; Beresneva, I. V.; Bykov, I. V.; Gainutdinov, R. V.; Koksharov, Y. A.; Mantsyzov, B. I.; Masselin, P.; Ozheredov, I. A.; Radchenko, I. L.; Shkurinov, A. P.; Tolstikhina, A. L. *Colloids Surf A* 2002, 198, 491.
15. Becker, P. C.; Olsson, N. A.; Simpson, J. R. *Erbium-Doped Fiber Amplifier*; Academic: New York, 1999.
16. Krumova, M.; Loez, D.; Benavente, R.; Mijangos, C.; Perena, J. M. *Polymer* 2000, 41, 9265.
17. McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967.
18. Koner, R.; Drew, M. G. B.; Figuerola, A.; Diaz, C.; Mohanta, S. *Inorg Chem Acta* 2005, 358, 3041.
19. Tamboura, F. B.; Haba, P. M.; Gaye, M.; Sall, A. S.; Barry, A. H.; Jouini, T. *Polyhedron* 2004, 23, 1191.
20. Tamboura, F. B.; Diop, M.; Gaye, M.; Sall, A. S.; Barry, A. H.; Jouini, T. *Inorg Chem Commun* 2003, 6, 1004.
21. Borek, J.; Osoba, W. *J Polym Sci Part B: Polym Phys* 1998, 36, 1839.
22. Kumler, P. L.; Machajewski, G. A. *Macromolecules* 1987, 20, 1060.
23. Daly, J. H.; Bunton, L. *J Mater Sci* 1983, 18, 2817.
24. Krumova, M.; Lopez, D.; Benavente, R.; Mijangos, C.; Perena, J. M. *Polymer* 2000, 41, 9265.
25. Narisawa, N.; Ono, K.; Murakami, K. *Polymer* 1989, 30, 1540.
26. Tang, Y. F.; Du, Y. M.; Shi, X. W.; Kennedy, J. F. *Carbohydr Polym* 2007, 67, 491.
27. Al-Tantawy, F.; Abedel-Kader, K. M.; Kaneko, F.; Sung, Y. K. *Eur Polym J* 2004, 40, 415.
28. Abdel-Kader, K. A. M.; Abdel-Hamied, S. F.; Mansour, A. B.; El-Lawindy, A. M. Y.; Al-Tantawy, F. *Polym Test* 2002, 21, 847.
29. Cassu, S. N.; Felisberti, M. I. *Polymer* 1997, 38, 3911.
30. Gauthier, M. A.; Luo, J.; Calvet, D.; Ni, C.; Zhu, X. X.; Garon, M.; Buschmann, M. D. *Polymer* 2004, 45, 8201.
31. Krumova, M.; Lopez, D.; Benavente, R.; Mijangos, C.; Perena, J. M. *Polymer* 2000, 41, 9265.
32. Guohua, Z.; Liu, Y.; Cuilan, F.; Min, Z.; Caiqiong, Z.; Zongdao, C. *Polym Degrad Stab* 2006, 91, 703.
33. Zrinyi, M.; Buki, L. A. *Polym Gel Network* 1997, 5, 415.
34. *Periodic Table of the Elements*, Sargent-Welch Scientific Co., Skokie, Illinois, 1968.
35. Seanor, D. A. *Electrical Properties of Polymers*; Academic: New York, 1982.
36. Sessler, G. M. *Electrets*; Springer-Verlag: Berlin, 1980.
37. Elliott, S. R. *Adv Phys* 1987, 36, 135.
38. Picke, G. E. *Phys Rev B* 1972, 6, 1572.
39. Bhatnagar, V. K.; Bhatia, K. L. *J Non-Cryst Solids* 1990, 119, 214.