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# NMR and Conductivity Study of Gelatin-Based Polymer Electrolytes

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*Nuclear Magnetic Resonance spectroscopy (NMR) and complex impedance spectroscopy have been used to study gelatin-based polymer electrolytes plasticized with glycerol and containing lithium perchlorate. The studied samples were prepared with salt concentration of 7.9 wt% and 10.3 wt%. Ionic conductivity of about $10^{-5}$ S/cm was obtained at room temperature for both samples. Lithium ($^7Li$) and proton ($^1H$) lineshapes and spin-lattice relaxation times were measured as a function of temperature. The $^7Li$ NMR relaxation results indicate that the ionic mobility in this system is comparable to those found in other plasticized polymer electrolytes.*

**Keywords:** conductivity; gelatin; gel electrolyte; NMR; polymer electrolyte



## INTRODUCTION

Polymer electrolyte systems are one of the interesting areas for scientific and technological development, due to their potential application to a wide variety of electrochemical devices, such as high-energy density batteries, fuel cells, sensors and electrochromic devices [1]. For this reason scientific attention has focused on the development of a polymer system with high ionic conductivity and good physical and chemical properties by either modifying very well known poly (ethylene oxide)-based systems (PEO) or introducing new polymers. PEO modifications are usually promoted by crosslinking reactions,

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which lead to the formation of networks, addition of plasticizers and inert fillers resulting in the formation of polymer blends and composites respectively [2–5]. Another strategy is the addition or grafting of PEO with other non-conducting polymer or the proposal of new conducting polymeric systems, which contain heteroatoms in their structure. An example of the letter are SPEs based on natural polymers like chitosan [6,7] or modified starch [8]. Natural polymers are very attractive to the development of new materials, due to their biodegrability, low production cost and good physical and chemical properties. As examples of natural polymer-based SPEs, grafted hydroxyetlhycellulose (HEC), modified starch or chitosan have been obtained and showed very good $Li^+$ ions conductivity values as high as $10^{-5}$ S/cm at room temperature [ref.]. Also small ECDs with good color/bleaching properties have been already realized with these SPEs [9,10].

A new ionic conducting system based on commercial gelatin has been recently proposed [11]. This system has showed very good ionic conductivity values of $4.5 \times 10^{-5}$ S/cm at room temperature and $3.6 \times 10^{-4}$ S/cm at 80°C, good electrochemical reversibility and very high transparency. These good spectro-electrochemical results have lead us to perform a more fundamental study by submitting the samples to NMR measurements. With this technique it is possible to obtain detailed information about ionic dynamics, diffusion coefficients and polymer chain mobility in polymer electrolytes systems [12–16]. In our previous NMR study of natural polymer-based SPEs, it was possible to confirm the predominance of the amorphous phase in the films obtained for HEC grafted with DPEO, as well the presence of the motional line-narrowing process and the single relaxation maximum in both $^1H$ and $^7Li$ nuclei [12]. In the samples obtained with glycerol plasticized starch, it was observed that the cation-proton interaction is smaller than that in the grafted systems and that the lithium has relatively high mobility in the plasticized samples, which is likely to be a result of the solvent dynamics, whereas starch acts as a polymer matrix for the electrolyte [8]. The present work reports the results of conductivity and $^1H$ and $^7Li$ NMR measurements as a function of temperature of the gelatin-based SPEs (GGL), which are mixed systems, i.e., grafted and plasticized at the same time.

## EXPERIMENTAL

The GGL electrolytes were prepared according to the following formula: 2 g of commercial uncolored gelatin (Oetker®) was dispersed in 15 mL of water and heated under magnetic stirring for a few minutes up to 50°C for complete dissolution. Next, 1.25 g of glycerol

as plasticizer, 0.25 g of formaldehyde (cross-linking agent) and lithium perchlorate were added to this solution under stirring. The concentrations of $LiClO_4$ in the two samples studied here were 0.3 g (7.9 wt%) and 0.4 g (10.3 wt%), respectively. This viscous solution was then cooled down to 30°C and poured on Petri plates to form transparent films. The obtained materials were characterized by differential scaning calorimetry to determine their glass transition temperatures (not showed here). The ionic conductivities were obtained by measurements of complex impedance A.C. using a Solartron model 1260, in a temperature ranging between 10°C and 80°C, from 1 MHz to 10 Hz, using an AC potential of 50 mV. The $^1$H NMR spin-lattice relaxation times ($T_1$) measurements were carried out on a pulsed NMR spectrometer equipped with a TECMAG NMR-kit, operating at 36 MHz in the temperature range of 180–360 K. The $^7$Li NMR lineshapes and spin-lattice relaxation times measurements were carried out on a Varian-400 MHz *Inova* NMR spectrometer operating at 155.4 MHz in the temperature range of 180–360 K. Saturation-recovery pulse sequence ($\pi/2$ pulse $\approx 1.5\,\mu$s) was employed to determine spin-lattice relaxation times. The $^1$H and $^7$Li magnetization recoveries toward equilibrium were found to be exponential throughout the entire temperature range.



## RESULTS AND DISCUSSION

Figure 1 shows the ionic conductivities of the GGL films with 7.9 and 10.3 wt% $LiClO_4$. The AC conductivities measurements were performed in a temperature range between 300 K and 356 K. The data show a linear increase of conductivity with the increase of temperature according to Arrhenius model and similar to those observed in hydroxyethylcellulose and starch-based polymer gel electrolytes [8,17]. The ionic conductivities at 300 K of the samples with 7.9 wt% and 10.3 wt% of Li were $1.1 \times 10^{-5}$ S/cm and $0.9 \times 10^{-5}$ S/cm, respectively. From the linear fitting of the experimental data the energy activation ($E_a$) values of 62.7 kJ/mol (0.65 eV) were obtained for both samples.

Figure 2 shows a temperature dependence of the $^1$H NMR spin-lattice relaxation rates ($T_1^{-1}$) of the GGL:$LiClO_4$ films. Above 180 K, the relaxation rate increases as the temperature increases up to a well-defined maximum value of $(T_1^{-1})_{max} \approx 18.5\,s^{-1}$ at 300 K for both sample. The main relaxation process is of dipolar origin and due to the thermal motion of protons in the solvating medium (i.e., polymer + plasticizer) which modulates the dipolar $^1$H$-^1$H interactions. It should be noted that the $^1$H relaxation times (measured at the same Larmor

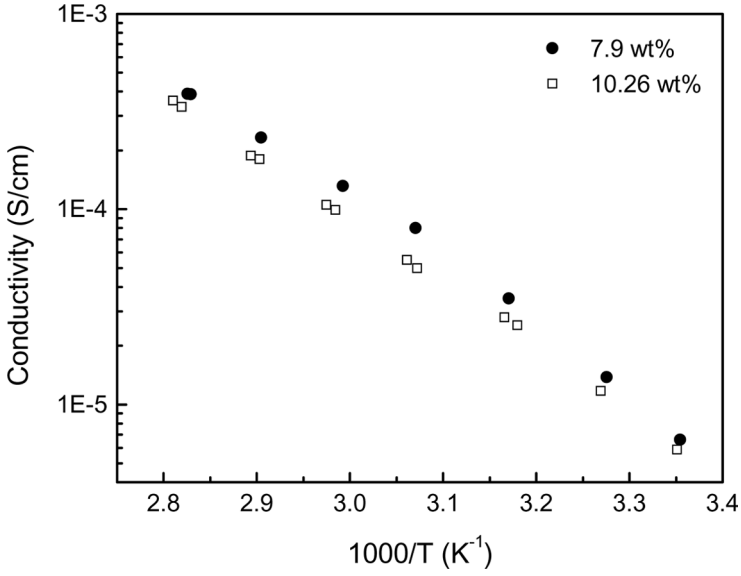


**FIGURE 1** Arrhenius plot of the ionic conductivity of the GGL:$LiClO_4$ electrolytes containing 7.9 wt% and 10.3 wt% lithium perchlorate.



frequency) in the electrolytes studied here are of the same order of magnitude as those observed in the plasticized HEC/$LiClO_4$/glycerol and in the starch-based electrolytes [8,17].

The temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ is usually analyzed using the simple Bloembergen, Purcell and Pound (BPP) model, which assumes non-correlated isotropic random motions [18]. In this context, the spectral density function is given by

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \tag{1}$$

The spin-lattice relaxation rate can be expressed in terms of the spectral density function evaluated at the NMR Larmor frequencies:

$$\frac{1}{T_{1D}} = C_1[J(\omega_I) + J(2\omega_I)] + C_2[J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)] \tag{2}$$

where $C_1 = 2\gamma_I^4 \hbar^2 I(I+1)/5r^6$ is the homonuclear coupling constant and $C_2 = 2\gamma_I^2 \gamma_S^2 \hbar^2 S(S+1)/5r^6$ is the heteronuclear one. The Larmor frequencies $\omega_I$ and $\omega_S$ refer to nuclei $I$ and S, respectively, under the same static magnetic field. In the case of the $^1$H resonance in polymer gel electrolyte, the $C_1$ is related the mean square amplitude of the

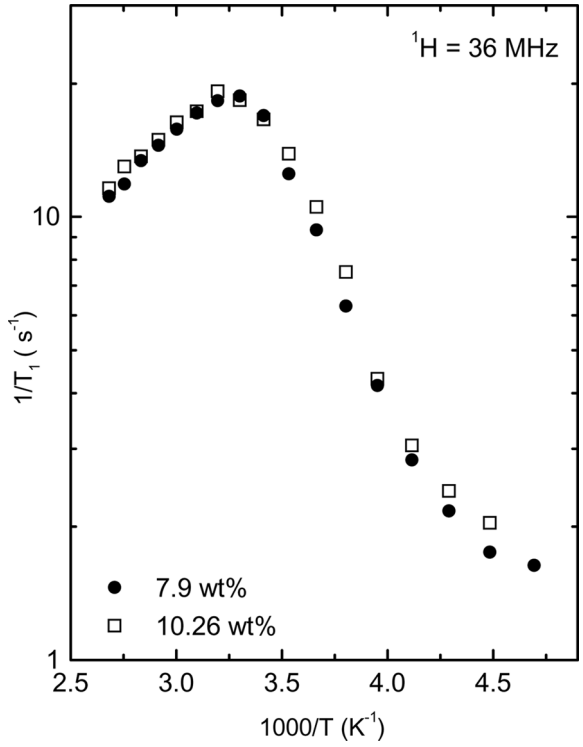


**FIGURE 2** Temperature dependence of the $^1$H spin-lattice relaxation rates $(1/T_1)$ in GGL:$LiClO_4$ measured at the Larmor frequency of 36 MHz.

fluctuation $^1H-{}^1H$ dipole-dipole interaction and the second term of the right side of equation (2) can be neglected. Equation (2) can be expressed as a function of temperature by assuming that the motions are ruled by a thermally activated process. An Arrhenius temperature dependence for $\tau_c$ is often assumed, $\tau_c = \tau_o \exp(E_a/k_B T)$, where $k_B$ is the Boltzman constant, $E_a$ is the activation energy and $\tau_o$ is the pre-exponential factor which is of the order of an optical phonon frequency $(10^{12} - 10^{14}\,s^{-1})$. Equation (1) predicts a maximum in $T_1^{-1}$ when $\omega_I \tau_c \approx 0.62$, therefore the position of relaxation rate maximum indicates the temperature at which the motional correlation time is comparable to reciprocal $^1$H Larmor frequency. The activation energies calculated from the linear slope of the $T_1^{-1}$ data in the low temperature side of the rate maximum are 0.21 eV for the film with 7.9 wt% Li and 0.22 eV for those with 10.3 wt% Li. Table 1 summarizes the parameters obtained from the $^1$H NMR spin-lattice relaxation data.

**TABLE 1** NMR Parameters Obtained from $^1$H Spin Lattice Relaxation Rate ($1/T_1$) in GGL:$LiClO_4$ Polymer Electrolytes with Different Li Concentrations; $T_{max}$ is the Maximum Relaxation and $E_a$ is the Activation Energy for the Motion Causing the Relaxation

| wt% of $LiClO_4$ | 7.9 | 10.3 |
|---|---|---|
| $T_{max}$(K) | 300 | 300 |
| $1/T_{1\,max}$ ($s^{-1}$) | 18.7 | 18.3 |
| $E_a$(eV) | 0.21 | 0.22 |
| $\tau_o$(s) | $8.5 \times 10^{-13}$ | $7.9 \times 10^{-14}$ |
| $\tau_c$(300 K) (s) | $2.8 \times 10^{-10}$ | $3.9 \times 10^{-10}$ |

Figure 3a shows the low temperature ($T = 183$ K) static $^7$Li NMR absorption spectrum for the GGL:$LiClO_4$ films. The spectrum is characterized by a broad line ($\Delta H \approx 30$ kHz) and a sharper central line ($\Delta H \approx 6.7$ kHz), where $\Delta H$stands for the full width at half maximum. Since nuclei with $I > 1/2$ have electric quadrupole moments, their NMR spectra and relaxation rates are usually dominated by the interaction of the nuclear quadrupole with the electric field gradients at the nucleus. The NMR powder spectrum of a nucleus with $I = 3/2$ (as $^7$Li) consists, up to the first order in the quadrupolar perturbation, of a

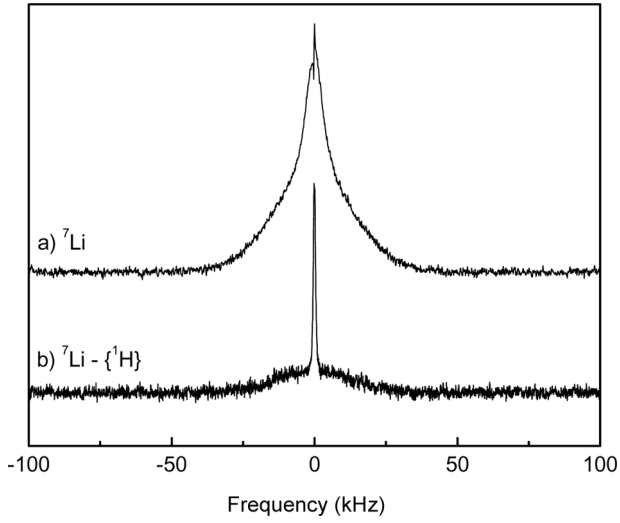


**FIGURE 3** $^7$Li NMR spectrum of the GGL:$LiClO_4$ obtained by Fourier transforming the FID NMR signal at 183 K. (a) $^7$Li NMR spectra and (b) $^7$Li-{$^1$H} decoupled spectra.

dipolar broadened central line associated with the $1/2 \leftrightarrow -1/2$ transition and a symmetric pattern due to the $3/2 \leftrightarrow 1/2$ and $-1/2 \leftrightarrow -3/2$ satellite transitions. Nevertheless, in polymer electrolytes, one usually observes a distribution of $\pm 3/2 \leftrightarrow \pm 1/2$ nuclear quadrupole satellite transitions, which is attributed to a distribution of electric field gradients at the lithium sites (i.e., a distribution of the quadrupolar coupling which smears out the quadrupole satellite structure) [7,8,12]. The proportions of the area of the central resonance to the area of the broad base of the resonance peak amounts to $\sim 30\%$ which, within the experimental error, agree with the theoretical value of 40% expected for a $I = 3/2$ spectrum with first-order quadrupole interaction [8,12].

The central line of the experimental spectrum in Figure 3a is not broadened (up to first order) by the quadrupole coupling, but other broadening sources, such as the homo- and the heteronuclear dipole-dipole couplings to neighboring nuclei, can contribute to its linewidth. Besides the homonuclear dipole–dipole broadening of the central line, there are heteronuclear contributions from protonic species.The homonuclear Li–Li and the heteronuclear Li–H dipolar contributions to the $^7$Li central line were determined by means of high-power proton decoupling NMR experiments. Figure 3b shows the $^7\text{Li}-\{^1\text{H}\}$ decoupled spectra at 183 K for the GGL:$LiClO_4$. A reduction in the $^7$Li linewidth from 6.7 kHz to 0.9 kHz is clearly visible, reflecting the strong interaction between $^7$Li and the protons of the gelatin and glycerol. It should be noted that the proton decoupling on the $^7$Li resonance in PEO and HEC-based SPEs yields a 80–90% reduction in the linewidth [12,17].

Figure 4 shows the $^7$Li NMR central transition linewidth as a function of the temperature for the polymer gel electrolytes obtained at a temperature range of 180 K at 370 K. Above 190 K, the mobility of the $Li^+$ ions increases enough to average out the magnetic and the electric interactions producing a line narrowing. The temperature of the line transition shifts to lower temperatures as the $LiClO_4$ concentration increases. The analysis of the line narrowing data in Figure 4 yields activation energies of 0.34 eV for the GGL:$LiClO_4$ with 7.9 wt% of $LiClO_4$ and 0.32 eV for the sample with 10.3 wt% $LiClO_4$. It should be noted that the differences between the activation energies extracted from the NMR data and those obtained from the conductivity meauseremements are most likely to be a result of the different time scale of the NMR measurements compared with conductivity meausurements [17].

Figure 5 shows the temperature dependence of the $^7$Li spin-lattice relaxation rates $T_1^{-1}$of the GGL:$LiClO_4$ samples. The $^7$Li relaxation rates increase almost two orders of magnitude between 220 K and 400 K, reflecting the high ion mobility in these electrolytes. The shapes

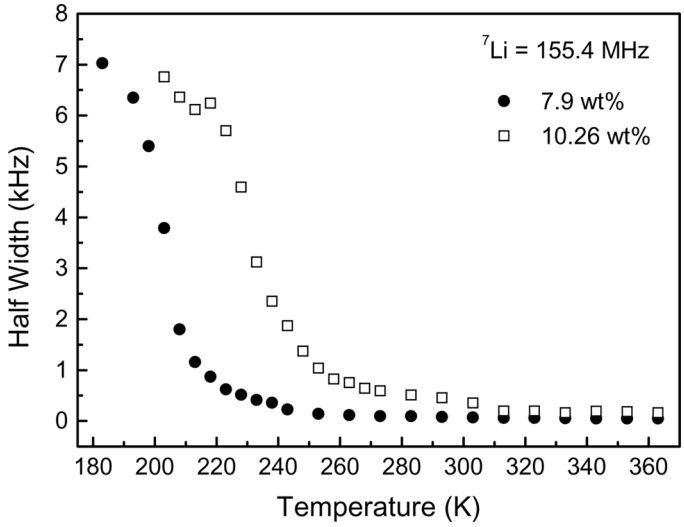


**FIGURE 4** Temperature dependence of the $^7$Li NMR central transition linewidth of the GGL : $LiClO_4$ electrolytes containing 7.9 wt% and 10.3 wt% lithium perchlorate.



of the relaxation curves are similar for both samples. A change in the slope of the $T_1^{-1}$ curve is observed near 300 K. According to M. Forsyth et al. [19,20], the lithium interaction in polymer gel electrolytes changes from $Li^+$-polymer to $Li^+$-solvent dominated by increasing temperature. Within this concept, a satisfactory interpretation of the relaxation data in Figure 5 can be achieved by assuming that there are at least two distinct lithium ion dynamics. The low-temperature relaxation process is characterized by activation energies of 0.36 eV for the GGL:$LiClO_4$ with 7.9 wt% $LiClO_4$ and 0.30 eV for the sample with 10.3 wt% $LiClO_4$, which is comparable with [ref].

The BPP model outlined above predicts the presence of a spin-lattice relaxation rate maximum at a given temperature, $T_{max}$, at which the condition $\omega_o\tau_c \approx 0.62$ is fulfilled. Since the $^7$Li Larmor frequency in our experiments is $\omega_o = 2\pi\ (155.4\,\text{MHz}) = 9.76 \times 10^8\,\text{s}^{-1}$, it is possible to obtain a value for the correlation time at the temperature of the rate maximum. Therefore, the position of the $T_1^{-1}$ maximum indicates the temperature at which the motional correlation time is comparable to the reciprocal Larmor frequency. One can compare the relative mobilities of the nuclei in different samples measured at the same Larmor frequency by comparing the temperature positions of the relaxation rate maxima. In solvent-free polymer electrolytes, the $^7$Li relaxation

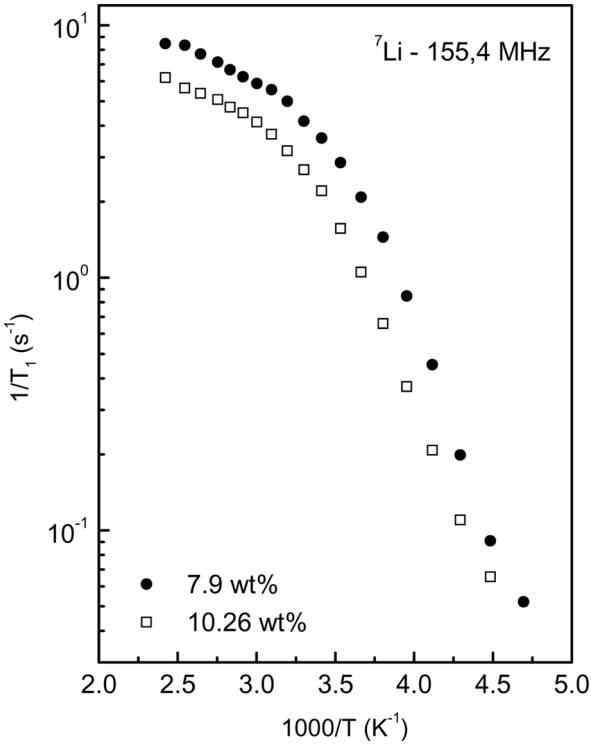


**FIGURE 5** Temperature dependence of the $^7$Li spin-lattice relaxation rates $(1/T_1)$ in GGL : $LiClO_4$ electrolyes measured at the Larmor frequency of 155.4 MHz.

rate associated with the mobile lithium ions reaches the maximum at $T_{max} \approx 350$–$360$ K when measurements are performed at 155 MHz [12,21]. Plasticized starch-based polymer electrolyte displays $^7$Li $T_1^{-1}$ maximum at lower temperatures ($T_{max} \approx 323$ K) [8]. It is evident from Figure 5 that the low temperature relaxation process stands from 220 K to 300 K in both samples. Although the $^7$Li$T_1^{-1}$ maxima are not observed, the temperature dependence of the NMR relaxation suggests that the lithium mobility in the gelatin-based electrolytes is comparable to those observed in the starch-based ones. Further work is in progress to confirm these results.

## CONCLUSIONS

This article reported the conductivity measurements and an NMR study of $^1$H and $^7$Li lineshapes and relaxation times in polymer

electrolytes formed by gelatin plasticized with glycerol and containing lithium perchlorate. The studied samples were prepared with salt concentration of 7.9 wt% and 10.3 wt%. Ionic conductivities of about $10^{-5}$ S/cm were obtained at room temperature for both samples. The temperature dependence of the $^{7}$Li spin-lattice relaxation suggests that there are two dynamic processes associated with lithium diffusion in the gelatin-based electrolytes studied here.

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