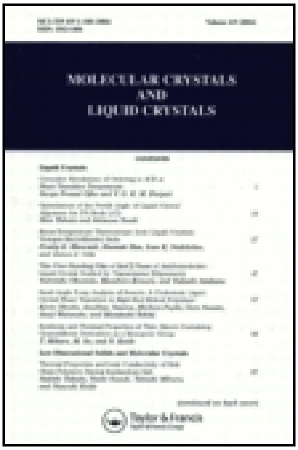

Molecular Crystals and Liquid Crystals

NMR and Conductivity Study of Starch BasedPolymer Gel Electrolytes

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NMR and Conductivity Study of Starch Based Polymer Gel Electrolytes

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Nuclear Magnetic Resonance spectroscopy (NMR) and complex impedance spectroscopy have been used to study the polymer gel electrolytes formed by amylopectin rich starch, plasticized with glycerol and containing lithium perchlorate. The use of plasticizer enhances the conductivity, which reaches $\sim 10^{-4}$ *S/cm at room temperature. The* ^{7}*Li NMR decoupling experiments performed at 183 K show that 80% of the sub-*T_g *linewidth is attributable to the heteronuclear Li-H interaction, suggesting a weaker Li – polymer interaction in the plasticized electrolyte when compared with the unplasticized ones. The Li-7 NMR results exhibit the qualitative features associated with the lithium mobility in the polymer gel electrolyte, namely the presence of a well defined Li-7 spin-lattice relaxation maxima at 340 K.*

Keywords: gel electrolyte; NMR; plasticizer; polymer electrolyte; starch

INTRODUCTION

Solid polymer electrolytes (SPE) have been extensively studied in the last two decades because of their potential use in technological applications, as solid-state batteries, and electrochromic devices [1–3]. The SPE obtained from natural polymers – as starch and cellulose derivatives – have been the object of a great deal of research because of their

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mechanical and electrical properties [4–7]. In recent years it has been found that the ionic conductivity of the polymer electrolytes can be considerably enhanced upon addition of plasticizers capable of complexing the lithium ion and a number of studies have addressed the NMR characterization of these SPE [7–10]. In previous papers, we reported the conductivity and nuclear magnetic resonance studies of SPE formed by amylopectin rich starch plasticized with 30% glycerol and containing lithium perchlorate (salt concentration $[O]/[Li] = 6$ and 8). The NMR results shows that the cation-proton interaction was smaller than that in grafted systems and that the relatively high mobility of the lithium ion was associated with the solvent dynamics [11]. In this communication, we report conductivity and ^{1}H and ^{7}Li NMR spin-lattice relaxation measurements as a function of temperature of the same polymer gel electrolyte plasticized with glycerol (30%) and containing lithium perchlorate with $[O]/[Li] = 10$.

EXPERIMENTAL

Polymer gel electrolyte were prepared using amylopectin rich starch, glycerol (30% of the starch mass) and lithium perchlorate. Further details of the sample preparation are given elsewhere [11]. The resulting films were characterized by DSC, TGA, XRD and scanning electron microscopy (SEM) techniques [6]. Glass transition temperatures (T_g) between 244 K and 261 K were determined for the electrolytes with [O]/[Li] between 6 and 10, i.e., lower than that of the amylopectin rich starch ($T_g \sim 323\,K$). Ionic conductivity was determined by complex impedance measurements in the temperature range 290–365 K using a Solartron 1260 equipment operating in the frequency range 10 Hz to 1 MHz. Proton (^{1}H) NMR lineshapes and spin-lattice relaxation time (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 220–400 K. The ^{7}Li NMR measurements were performed in a Varian-400 MHz *Inova* NMR spectrometer operating at a ^{7}Li-resonance frequency of 155.4 MHz. The heteronuclear dipolar interactions (mainly Li-H) were removed from the ^{7}Li spectra by use of the decoupling technique by exciting the ^{1}H nuclear system with the Larmor frequency of 400 MHz.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the ionic conductivity (σ) for the amylopectin/$LiClO_4$/glycerol samples with concentration $[O]/[Li], n = 10$. Above 300 K the conductivity increases with increasing

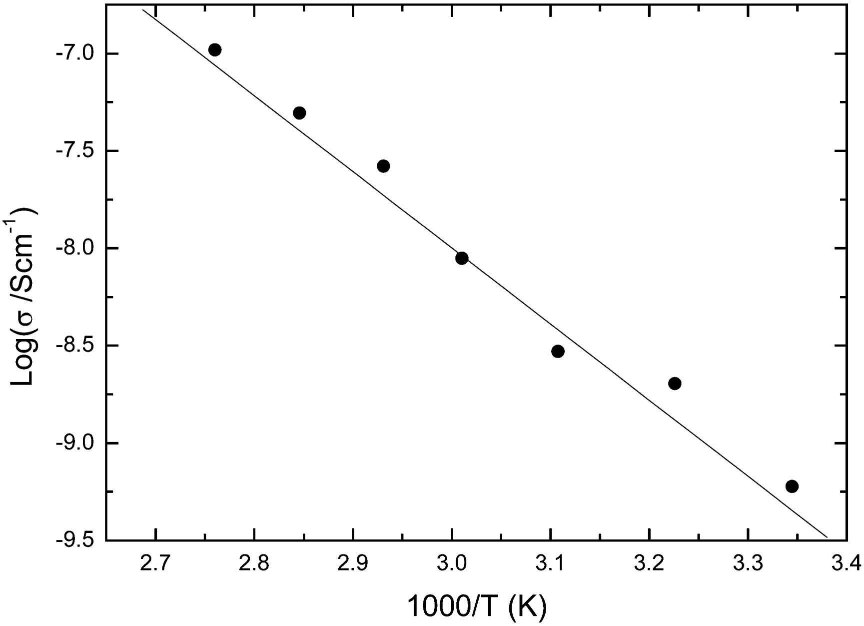

FIGURE 1 Arrhenius plot of ionic conductivity of the amylopectin/$LiClO_4$/glycerol polymer gel electrolyte containing 30% of glycerol and [O]/[Li] = 10.

temperature, reaching values of $\sigma \approx 10^{-3}$ S/cm at 365 K. Such values are of the same order of magnitude than those found in plasticized polymer electrolytes [8,10]. The conductivity display an Arrhenius behavior over all the reported temperature range, resulting in activation energies E_a of 0.35 eV (Fig. 1). The value of E_a suggests that the $LiClO_4$ salt was totally dissolved and the complex was amorphous.

The ^{1}H static NMR spectra recorded at low temperature (173 K) of the polymer gel electrolyte with 30% of glycerol consists of a central line of flanked by a pair of peaks separated by ~11 Gauss. The side peaks conform a Pake doublet [12] which can be attributed to a pair of protons ~2 Å apart in the glycerol and in the starch. The central line can be attributed to the superposition of the ^{1}H signals belonging to the OH and CH groups of the glycerol. Above ~220 K, the central resonance line narrow upon increasing temperature due to the averaging of the ^{1}H dipole-dipole interactions caused by the increase in proton mobility. This line transition seems to be associated to the onset of the reorientational dynamics of the glycerol molecule [13].

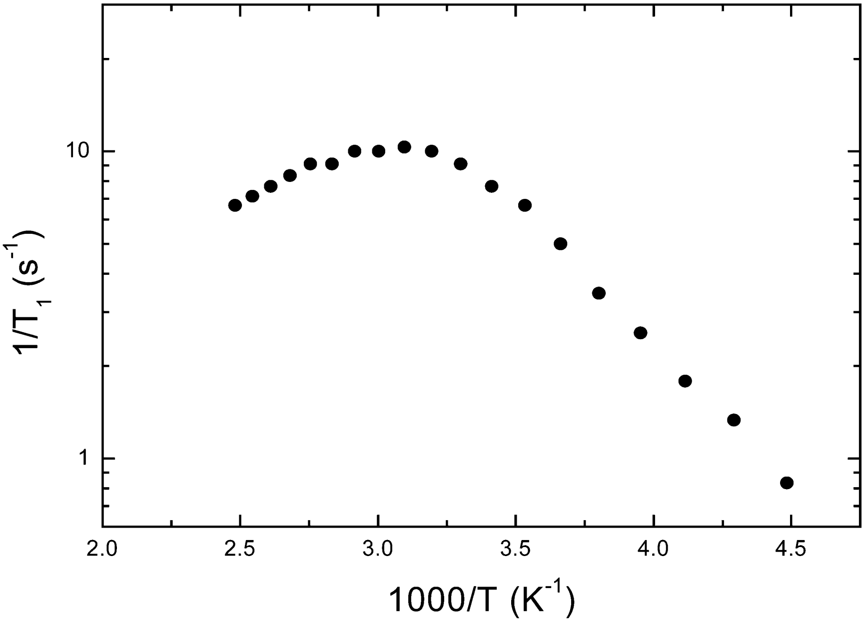

FIGURE 2 Temperature dependence of the ^{1}H spin-lattice relaxation rates (T_1^{-1}) in amylopectin/LiClO$_4$/glycerol gel electrolytes with 30% glycerol, measured at the Larmor frequency of 36 MHz.

Figure 2 shows the temperature dependence of the proton spin-lattice relaxation rates (T_1^{-1}) of the polymer gel electrolyte measured at 36 MHz. The proton relaxation process can be interpreted in terms of the fluctuations of the strong ^{1}H-^{1}H dipolar interactions between protons presented in the solvating medium (i.e., polymer + plasticizer). The data in Figure 2 display a single relaxation rate maximum at $T_{\max} \approx 323$ K. The linear dependence of the logarithm of (T_1^{-1}) on the inverse temperature observed in the temperature range 220–290 K (Fig. 2) allow the determination of the activation energy of the process responsible for proton relaxation, $E_a \approx 0.19$ eV, which is of the same order than those obtained in starch- and hydroxyethylcellulose- based gel electrolytes ($E_a \approx 0.14$–0.24 eV) [11,14]. It should be noted that the proton mobility of the pure amylopectin is very low. NMR spin-lattice relaxation measurements in the rotating frame between 100 K and 300 K of amorphous polysaccharides indicate a relative lower mobility: the correlation time for the proton motion at room temperature ($\tau \sim 10^{-5}$ s) was much higher than those found in the amylopectin/LiClO$_4$/glycerol gel electrolyte studied here ($\tau \sim 9 \times 10^{-9}$ s). This value

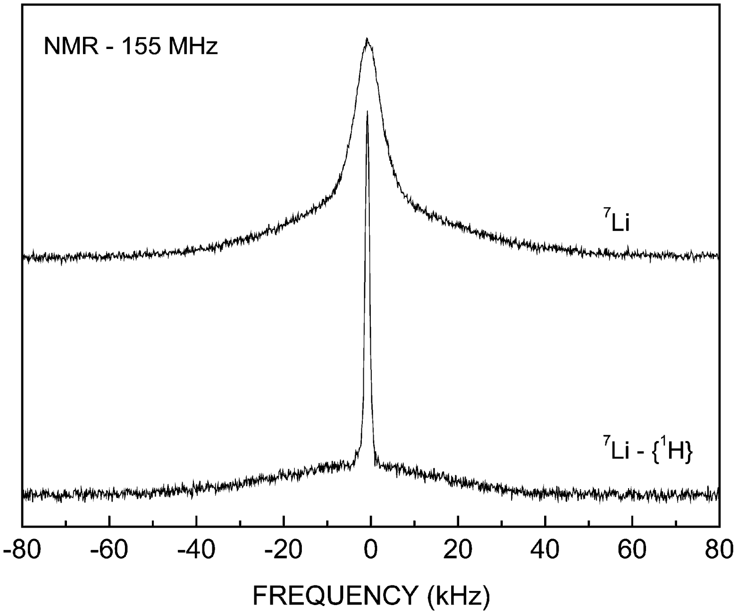

FIGURE 3 ^{7}Li NMR spectrum of amylopectin/LiClO$_4$/glycerol polymer gel electrolyte recorder at 183 K (upper figure) and ^{7}Li-{^{1}H} decoupled spectra (bottom figure).

however, is comparable to the proton correlation time of the rotational motions of the glycerol molecules, $\tau(300\,\mathrm{K}) \sim 10^{-9}$ s [13].

The low temperature (183 K) ^{7}Li NMR absorption spectrum (spin $I = 3/2$) of amylopectin/LiClO$_4$/glycerol ($n = 10$), is shown in Figure 3. The NMR powder spectrum of a nucleus with $I = 3/2$, such as ^{7}Li, consists, up to first order in the quadrupolar perturbation, of a central line associated with the $1/2 \leftrightarrow -1/2$ transition and a symmetric pattern due to the $3/2 \leftrightarrow 1/2$ and $-1/2 \leftrightarrow -3/2$ transitions [12]. The measured ^{7}Li spectra of the gel electrolytes at $T < 170$ K show a lineshape consisting of a relatively narrow central line (full width at half maximum $\Delta H \approx 7$ kHz) superimposed on a broad base line ($\Delta H \sim 44$ kHz), which is attributed to a distribution of $\pm 3/2 \leftrightarrow \pm 1/2$ nuclear quadrupole satellite transitions [5,14]. For nuclear spins $I > 1/2$ with small quadrupolar moment, such as ^{7}Li, the central transition linewidth is primarily determined by heteronuclear Li-H dipole-dipole couplings to neighboring protons in the amylopectin starch and the plasticizer (glycerol). In order to investigate such interactions, heteronuclear decoupling experiments were performed at low temperature (183 K). The ^{7}Li-{^{1}H} decoupled spectra (Fig. 3, bottom) demonstrate that 80% of the sub-T_g linewidth is attributable to the heteronuclear ^{7}Li-^{1}H interaction. The reduction in the ^{7}Li linewidth from 7.1 kHz to 1.4 kHz (Fig. 3) reflects the strong interaction between the ^{7}Li and the protons of the amylopectin and glycerol.

Above 170 K, the mobility of the Li^+ ions increases enough to average out the magnetic and the electric interactions producing a line narrowing. Figure 4 shows the temperature dependence of the ^{7}Li central transition line-width in amylopectin/$LiClO_4$/glycerol gel electrolytes. The onset of the line-narrowing, which heralds the presence of Li^+ ion motion on a time scale comparable to the reciprocal of the ^{7}Li NMR line-width ($\sim 10^{-5}\,s^{-1}$), occurs close to the calorimetric T_g ($\sim$223 K). In polyether-salt polymer electrolytes there exists a well-established correspondence between the calorimetric glass transition temperature and the onset of the ^{7}Li motional narrowing. The correspondence was considered a strong indication of the coupling of Li^+ to the ether oxygens and, therefore, to the segmental motion of the polymer chains, which become relevant at the glass transition [14].

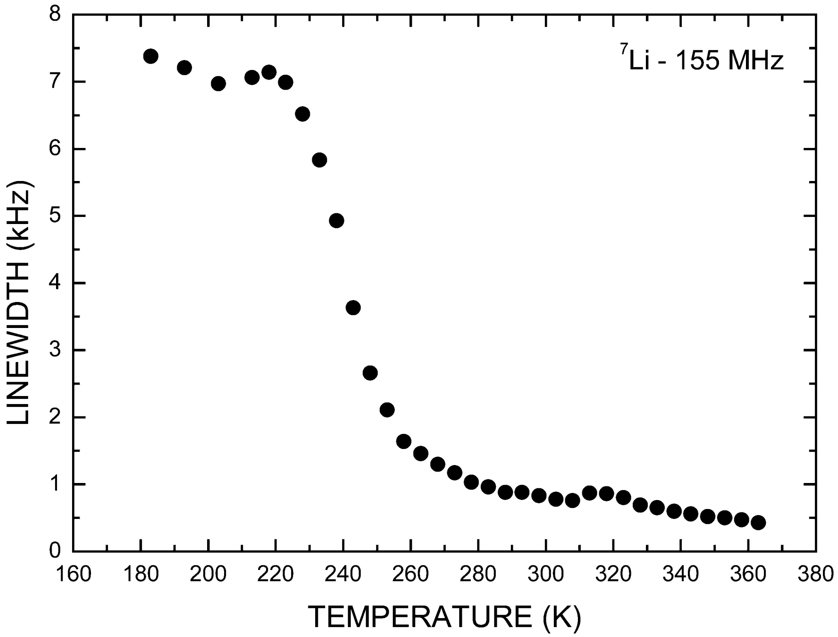

FIGURE 4 Temperature dependence of the ^{7}Li NMR central linewidth for amylopectin/$LiClO_4$/glycerol polymer gel electrolytes with 30% of glycerol.

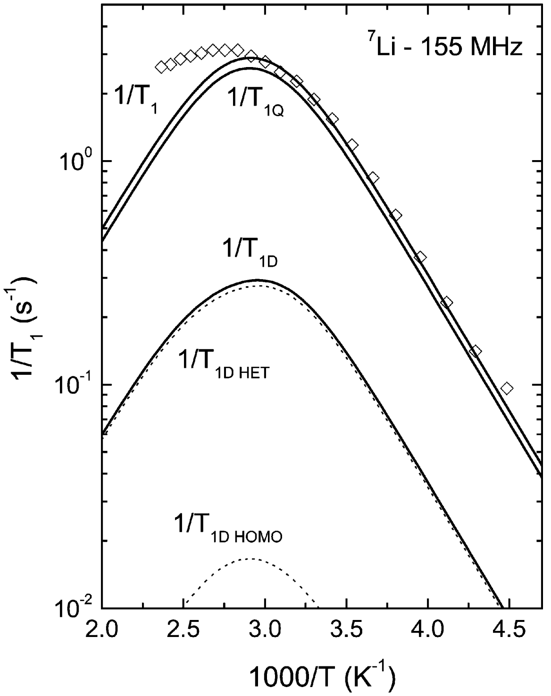

FIGURE 5 Temperature dependence of the ^{7}Li spin-lattice relaxation rates (T_1^{-1}) in amylopectin/LiClO$_4$/glycerol polymer gel electrolytes with 30% of glycerol, measured at the Larmor frequency of 155.4 MHz.

Figure 5 shows the temperature dependence of the ^{7}Li spin-lattice relaxation rates (T_1^{-1}) of the Amylopectin/LiClO$_4$/glycerol gel electrolyte. The ^{7}Li (spin $I = 3/2$) NMR relaxation in polymer electrolytes is mainly governed by two mechanisms: (i) quadrupolar relaxation due to the interaction between the quadrupole moment of the ^{7}Li nuclei and the fluctuating electric field gradient produced by the surrounding electrical charge distribution and (ii) the dipolar relaxation produced by random fluctuations of the lithium homo and heteronuclear dipole-dipole interactions. The former interaction is the dominant relaxation mechanism in solvent-free polymer electrolytes [7,10]. The ^{7}Li relaxation rate is observed to reach a maximum at $T_{\max} \approx 340$ K (Fig. 5). The ^{7}Li T_1^{-1} maximum (measure at the same Larmor frequency) in solvent-free polymer electrolytes are typically observed around 350–360 K. The position of the relaxation rate maximum suggests that there are little enhancement of the lithium mobility when the plasticizer was introduced in the electrolyte.

The temperature dependence of the relaxation rate T_1^{-1} is usually analyzed using the simples Bloembergen, Purcell and Pound (BPP) model, which assume non-correlated isotropic random motions, yielding to exponential time dependence for the nuclear spin correlation function [12]. In this context, the spectral density function, $J(\omega)$, given by the Fourier transform of the spin correlation function,

$$J(\omega_o) = \frac{\tau}{1+\omega_o^2\tau^2} \tag{1}$$

This spectral density function Eq. (1), is parameterized by the correlation time (τ) of the molecular motion modulating the nuclear spin interactions. An Arrhenius behavior is often assumed for the correlation time, $\tau = \tau_o \ \exp(E_A/k_B\ T)$, were k_B is the Boltzmann constant, E_A the activation energy and τ_o is a pre-exponential factor. The spin-lattice relaxation rate can be expressed in terms of the spectral density function evaluated at the NMR Larmor frequency, ω_o and at its first harmonics, $2\omega_\mathrm{o}$, [12]

$$\frac{1}{T_1} = C[J(\omega_o) + J(2\omega_o)] \tag{2}$$

where C is a constant which depends on the spin interaction responsible for the relaxation (i.e., dipolar or quadrupolar coupling). An estimate of the dipolar contribution to the spin-lattice relaxation rate, $(T_1^{-1})_d$, can be obtained from the lithium second moment, by using the expression $(T_1^{-1})_d \approx C_d\gamma^2 M_2/\omega_o$, where ω_o is the ^{7}Li Larmor frequency and C_d is a constant of the order of unity. Considering the line-width of the central line measured with and without ^{1}H decoupling, the corresponding homo and heteronuclear contribution to the second moment can be obtained. Since the measured ^{7}Li relaxation rate results from both, dipolar and quadrupolar contributions, $T_1^{-1} = (T_1^{-1})_d + (T_1^{-1})_q$, the quadrupolar contribution can be estimated. Figure 5 shows the fitting of Eq. (2) to the experimental data, obtained with a homo and heteronuclear dipolar constant, $C_d \approx 0.11 \times 10^8\ \mathrm{s}^{-2}$ and $3.5 \times 10^8\ \mathrm{s}^{-2}$, respectively, and the quadrupole one, $C_Q \approx 1.8 \times 10^9\ \mathrm{s}^{-2}$. The resulting quadrupole coupling constant, $\nu_\mathrm{Q} = 21\,\mathrm{kHz}$, is of the same order of magnitude than those obtained from the half-width of the broad base line in Figure 3, which is a reasonable estimate of the mean nuclear quadrupole coupling constant. The activation energy calculated from the linear slope of the ^{7}Li relaxation in Figure 4 yields $E \approx 0.24\,\mathrm{eV}$ and the pre-exponential factor of the Arrhenius expression is $\tau_\mathrm{o} \approx 2 \times 10^{-13}$ s.

It is well known that the addition of plasticizers enhances the ionic conductivity of the polymer gel electrolytes improving the salt dissiociation, decreasing ion pairing and increasing the number of charge carriers [8,10,14]. The ^{7}Li NMR results suggest that these factors must be associated with the decoupling of the lithium ion dynamics. According to M. Forsyth *et al.* [8], the lithium interaction in polymer gel electrolytes changes from being Li-polymer to be Li-solvent dominated with increasing temperature.

CONCLUSIONS

This paper reports an NMR and complex impedance spectroscopy study of the polymer gel electrolytes formed by amylopectin rich starch, plasticized with glycerol and containing lithium perchlorate. The conductivity results indicate that use of plasticizer enhances the conductivity, which reaches $\sim 10^{-4}$ S/cm at room temperature. The ^{7}Li NMR decoupling experiment shows that 80% of the sub-T_g line-width is attributable to the heteronuclear Li-H interaction. The onset of the ^{7}Li line-narrowing, which heralds the presence of Li^+ ion motion on a time scale comparable to the reciprocal of the ^{7}Li NMR line-width ($\sim 10^{-5}$ s^{-1}), occurs close to the calorimetric T_g ($\sim$223 K). The Li-7 NMR results exhibit the qualitative features associated with the lithium mobility in the polymer gel electrolyte, suggesting that these gel eletrolytes can be potentially useful for SPE applications.

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