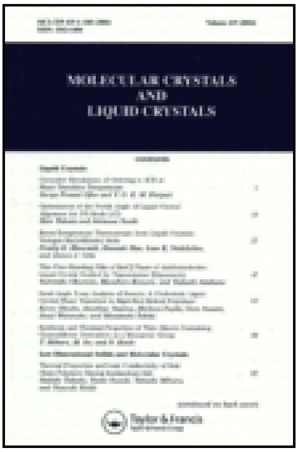

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NMR Study of the Polymer Electrolyte Formed by Ethylene Glycol, Citric Acid and $LiClO_4$

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In this work we report a proton (^1H) and lithium (^7Li) NMR lineshape and spin-lattice relaxation time investigation of this polymer electrolyte obtained from the polymerization of ethylene glycol and citric acid with lithium salt. The ^7Li data indicates that the lineshape and spin-lattice relaxation is affected by the coupling of its quadrupolar moment to the surrounding electric field gradients. The activation energy for the lithium motion extracted from the ^7Li relaxation data is 0.23 eV. The dynamics parameters obtained from the NMR data indicate that the lithium mobility in the EG:CA:$LiClO_4$ is comparable to those found in polymer gel electyrolytes and in plasticized polymer electrolytes.

Keywords: NMR, Polymer Electrolyte, Gel Electrolyte

INTRODUCTION

Polymer electrolytes (PE) are the subject of significant academic and technological interest, partly because of their proposed large-scale use in secondary lithium batteries and electrochromic devices, and partly because of the remarkable mechanism of ionic transport in disorder media [1,2]. The ionic conductivity of PE is due to the motion of dissolved ionic species in a polymeric matrix. The polyester formed between ethylene glycol (EG) and citric acid (CA) has been used as a polymer precursor in the preparation of ceramic oxides [3]. In this paper we report an investigation of ^1H and ^7Li NMR line shapes and spin-lattice relaxation times of the liquid polymer electrolyte obtained from the polymerization of EG and CA with the lithium salt $LiClO_4$.

EXPERIMENTAL

The viscous polymer electrolyte sample ($\eta \sim 582$ cp) was prepared by dissolving ethylene glycol and citric acid (CA:EG = 1:4). The polymerization was performed at 110° C for 2 hours [3]. Appropriate amounts of polymer and salt ($LiClO_4$) were weighed and dissolved to the desired $LiClO_4$:CA ratio of 1:10. Proton (^1H) NMR measurements were carried out on a pulsed NMR spectrometer operating at 36 MHz and the ^7Li NMR measurements were performed on a Varian-400 MHz *Inova* spectrometer operating at 155.4 MHz. The ^7Li magnetization recoveries to its equilibrium value were found to be exponential throughout the whole temperature range studied.

RESULTS AND DISCUSSION

The low temperature (180 K) ^7Li spectrum for the EG/CA:$LiClO_4$ polymer electrolyte is shown in Figure 1 (insert). The spectrum is characterized by a low intensity broad line ($\Delta H \sim 30$ kHz) and a sharper central line ($\Delta H \sim 6$ kHz), whereΔH stands for the full width at half maximum. The NMR spectrum of a spin $I = 3/2$ system (as ^7Li) in a powdered crystalline sample consists of a narrow component due to the ½ ↔ -½ transition and a doublet due to the ±3/2 ↔ ±1/2 transitions. Nevertheless, in polymer electrolytes, one usually observes a distribution of ±3/2 ↔ ±1/2 nuclear quadrupole satellite transitions resulting in broad shoulders flanking the central line. This behavior is attributed to a distribution of electric field gradients at the lithium sites, which may be due to the heterogeneous Li-polyester configuration in the polymer electrolyte [4]. The NMR spectrum is essentially unchanged until approximatelly 200 K at which point the broad shoulder and the central transition begins to narrow (Fig. 1). The onset of line-narrowing, which indicates the presence of Li^+ ion motion on a time scale comparable to the reciprocal of the rigid lattice linewidth ($\Delta H_{RL} \sim 6.3$ kHz). A similar line narrowing is observed above ~ 180 K for the ^{1}H in the EG/CA:$LiClO_4$ sample when the mobility of the polymer chains increase enough to average out the intermolecular dipole interactions. Motional narrowing in polyether-salt polymer electrolytes is well established and underline the coupling between ionic and polymer segmental mobility in those systems [4,5]. The activation energy of the line narrowing process yields $E_A \approx 0.37 \pm 0.03$ eV.

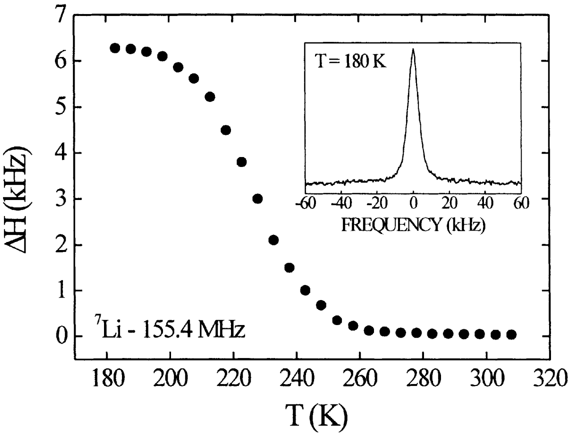

FIGURE 1 Temperature dependence of the ^{7}Li NMR central transition linewidth in of EG/CA:$LiClO_4$. Insert: ^{7}Li spectrum at 180K.

The temperature at which the ^{7}Li linewidth reduction occur can be estimated from the line narrowing condition. The line transition is expected when the correlation time of the ionic motion is about equal to the inverse of the linewidth, e.i. $\tau_c \approx 1/(\gamma^2 M_2)^{1/2}$. An estimate of the lithium second moment M_2, can be obtained from the measured width at half-maxima of the Gaussian line shape at 180 K (7.6 ± 0.4 kHz), yielding M_2 (Li) = 3.8 ± 0.4 G^2. Substituting of M_2 (Li) and the correlation time τ calculated with $E_A \approx 0.37$ eV and the pre-factor $\tau_o = 7 \times 10^{-15}$ s extracted from the relaxation data (see bellow), the ^{7}Li motional narrowing can be predicted at 190 K. The onset of motional narrowing is indeed observed at ~ 200 K (Fig.1).

Figure 2 shows the temperature dependence of the ^{1}H spin-lattice relaxation rates (T_1^{-1}) of EG/CA and EG/CA:$LiClO_4$. As show in Fig. 2, T_1^{-1} increases with increasing temperature up to a maximum value of 28 s^{-1} at approximately 255 K for EG/CA ($(T_1^{-1})_{max} \approx 17$ s^{-1} at 286 K for the electrolyte). The source of the proton relaxation in these systems is the random fluctuations of the ^1H-^1H dipole interaction caused by the polymer chain motions, and the relaxation rate T_1^{-1} maximum correspond to fluctuation rate of the order of the ^1H Larmor frequency, 36 MHz.

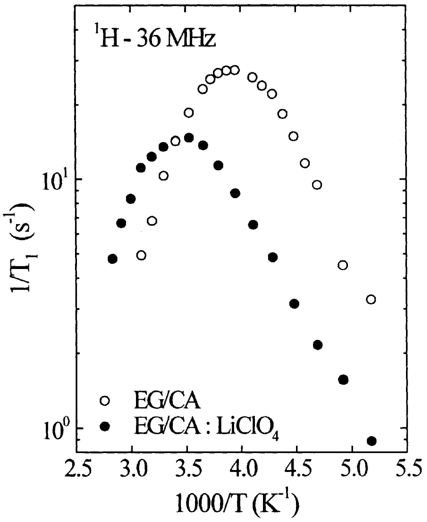

FIGURE 2 Temperature dependence of ^1H spin-lattice relaxation rates T_1^{-1} for EG/CA and EG/CA:LiClO$_4$ measured at 36 MHz.

The shift observed in the position of the relaxation rate maxima of EG/CA and EG/CA:LiClO$_4$ in Fig. 2 reflects the reduction of chain mobility when salt is dissolved in the polymer complex. The activation energy for the chain motion calculated from the linear slope of the ^1H T_1 data on the high temperature side of the rate maxima in Fig. 2 is $E_a \approx 0.27 \pm 0.04$ eV for EG/CA, which is consistent with the values reported for amorphous PEO ($E_a \approx 0.29$ eV) [6] and for PEG ($E_a \approx 0.28$ eV) [7].

Figure 3 shows the temperature dependence of the ^7Li spin-lattice relaxation rates of EG/CA:LiClO$_4$. T_1^{-1} peaks at 305 K, at which the lithium motional correlation time τ_c is comparable to the reciprocal of the Larmor frequency ω_o. The ^7Li NMR relaxation in polymer electrolytes are mainly governed by two mechanisms: (i) quadrupolar relaxation, $(T_1^{-1})_Q$ due to the interactions between the quadrupole moment of the ^{7}Li nuclei and fluctuations in the surrounding electric-field gradients produced by the charge distribution at the site of the nucleus, and (ii) the dipole relaxation $(T_1^{-1})_{dip}$ produced by random fluctuations of the lithium (Li-Li) and (Li-H) dipole interactions.

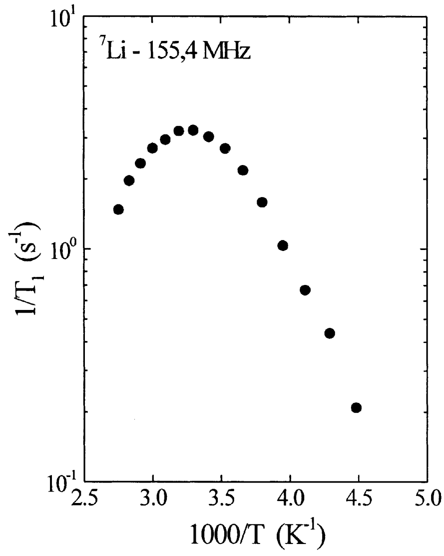

FIGURE 3 Temperature dependence of the ^{7}Li NMR spin-lattice relaxation rates in EG/CA:LiClO$_4$ measured at 155.4 MHz.

Using the expression for quadrupolar relaxation in the extreme narrowing limit in ref. 8, with $C_q \sim 30$ kHz (as estimated from the broad base line in Fig. 1, insert), and $\tau_c \sim 1/\omega_o \approx 10^{-9}$ s, we obtain T_1 $min \approx 0.28$ s, which compare well with the value experimentally observed at 305 K, $T_1 \approx 0.30$ s. This result indicates that quadrupolar interaction dominate the ^{7}Li spin-lattice relaxation.

The activation energy extracted from the linear slope of the ^{7}Li relaxation data in Fig. 3 on the low temperature side of the rate maximum (0.23 eV) is consistent with those reported in LiClO$_4$-based polymer electrolytes, 0.2 - 0.4 eV [9]. The constant $\tau_o \approx 7 \pm 3 \times 10^{-15}$ s, is determined from the relaxation rate maximum condition $\omega_o \tau_c \approx 1$.

In order to compare the mobility of the lithium ion in the electrolyte EG/CA:$LiClO_4$ with those found by NMR in other electrolytes, we estimated the correlation time τ_c for the lithium motion responsible for the ^{7}Li relaxation. The result, $\tau_c \approx 2\text{-}6 \times 10^{-10}$ s above 280 K, is close to those found for $PEG_{11}LiCF_3SO_3$ ($\tau_c \approx 7\text{-}10 \times 10^{-10}$ s) [6] and 3PEG:LiTf /DMF, where DMF is dimethyl formamide ($\tau_c \approx 8\text{-}11 \times 10^{-10}$ s) [10]. This result indicates that the relative mobility of the cation in the electrolyte EG/CA:$LiClO_4$ is comparable to those observed in gel electrolytes or plasticized polymer electrolytes.

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