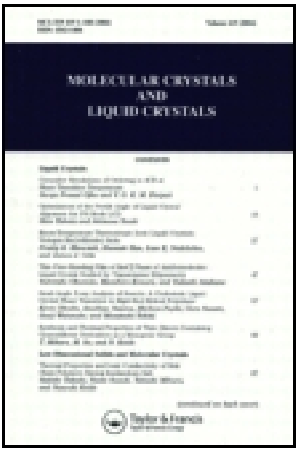

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DIELECTRIC RELAXATION IN PEO-MX SOLID ELECTROLYTES

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Abstract Poly(ethylene oxide) (PEO) complexed with salts has been shown to be characterized by a fair room temperature conductivity, high enough to allow technological applications. Dielectric Relaxation analysis technique is applied to study structural and transport properties of a number of normal and cross-linked PEO-based polymeric films.

INTRODUCTION

Polymer-based solid electrolytes are of growing importance in solid state electrochemistry because of their applications, the most important of which is for high-energy density batteries. These materials are attractive because their reversible elastomeric properties seem to make them ideal for cells using intercalation electrodes, which undergo significant changes in volume during charge and discharge cycles. During the last decade a wide, systematic work has been made to measure the ionic conductivity of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), pure or complexed with salts. In particular, it has been shown that PEO, due to its dielectric constant, is able to dissolve inorganic salts to form electrolytes with conductivity high enough to allow electrochemical applications [1]. PEO-complexed polymers, as pure PEO, are partially crystalline in nature, and the degree of crystallinity depends on the nature of the salt, its concentration, thermal history and aging. On the other hand, it is fully accepted that the ionic conductivity is primarily due to the amorphous elastomeric regions [2], so it is crucial to have a good knowledge of the conditions that determine the formation of the different phases and regulate the recrystallization processes. In order to hinder recrystallization, for example, attempts have been made to introduce cross-links into the amorphous phases, either with chemical methods [3], or with exposure to high energy radiations [4-5].

Dielectric Relaxation (DR) analysis is a well suited technique to study the ion-conducting polymers from this point of view; while the real part of the complex dielectric constant (the permittivity) plays a fundamental role in dissolving salts and in inhibiting crystal formation, the imaginary part (dielectric loss) it is a good probe for a number of phenomena, like the relaxations associated with local motions of polymer chains or the glass transition.

This work compares, for a wide range of temperatures and frequencies, the dielectric properties (complex dielectric constant and tan δ) and the ionic conductivity of pure and variously complexed PEO films, normal or γ-irradiated. An attempt is made to assign the relaxation phenomena that appear in the dielectric spectrum.

EXPERIMENTAL DETAILS

Pure PEO (B.D.H., M.W. = 6 M), was kept for 48 hours under vacuum (10^{-2} torr) at ~60 °C before use. A thin film (~100 μm) of PEO was prepared from acetonitrile (C. Erba, R.P.E.), cast on a teflon plate ad kept for 48 hours under vacuum at 60 °C. Not-irradiated films of the complex PEO_n–$LiClO_4$ (n = 8, 20) were obtained as previously described [6]; the film for n = 8 was prepared directly by casting on the dielectric sensor (see below). Not-irradiated films of PEO_{20}–$LiBF_4$ and PEO_{20}–$Pb(ClO_4)_2$ were prepared as described in [7] and [8], respectively. Finally, films of γ-irradiated PEO and PEO_n–$LiClO_4$ (n = 8, 20) were prepared as described in [4]. All samples (of thickness between 100 and 800 μm) were kept into a desiccator before performing the analyses.

The DR measurements have been made with a Dielectric Analyzer (DEA) 2970 by TA Instruments (USA), interfaced with a 80386 PC-based TA 2000 Analysis System. The DEA 2970 may perform the measurements at frequencies from 10^{-3} to 10^5 Hz, over a large temperature interval (−150 °C ÷ +500 °C). The samples (thin films in our case) are placed between two parallel sensors (gold-plated alumina) with a guard ring and a platinum thermocouple; the force acting over the electrodes may be programmed from 0 to 500 N, and continuously monitored. A micrometric Linear Variable Differential Transformer (LVDT) at any time measures the thickness of the sample. Before performing the experiments, the samples were kept at a temperature of 80 °C under dry nitrogen for 15 min, then a ramp was executed at a rate of 5 °C / min to −150 °C; after an isotherm 1 minute long, a final ramp at the same rate of 5 °C / min was executed to 80 °C. No relevant differences have been observed between cooling and heating cycles.

RESULTS AND DISCUSSION

Figures 1 and 2 show the decimal logarithm of the conductivity vs. the absolute temperature, at various frequencies, for normal (n-PEO) and γ-irradiated pure PEO (γ-PEO), respectively. The conductivity of γ-PEO, as already stated in literature [4-5], is more than one order of magnitude greater than that of PEO. In both cases, it is possible to recognize a region dominated by an Arrhenian behaviour (under the glass transition temperature, T_g) and a region, at higher temperature, where the conductivity roughly obeys the Vogel-Tamman-Fulcher (VTF) [9] or the equivalent Williams-Landel-Ferry (WLF) [10] law. In addition, while the γ-PEO conductivity exhibits only a little dispersion over the T_g, the n-PEO plot is strongly frequency-dependent and seems to be characterized by a thermally-activated relaxation mechanism contributing to the overall conductivity.

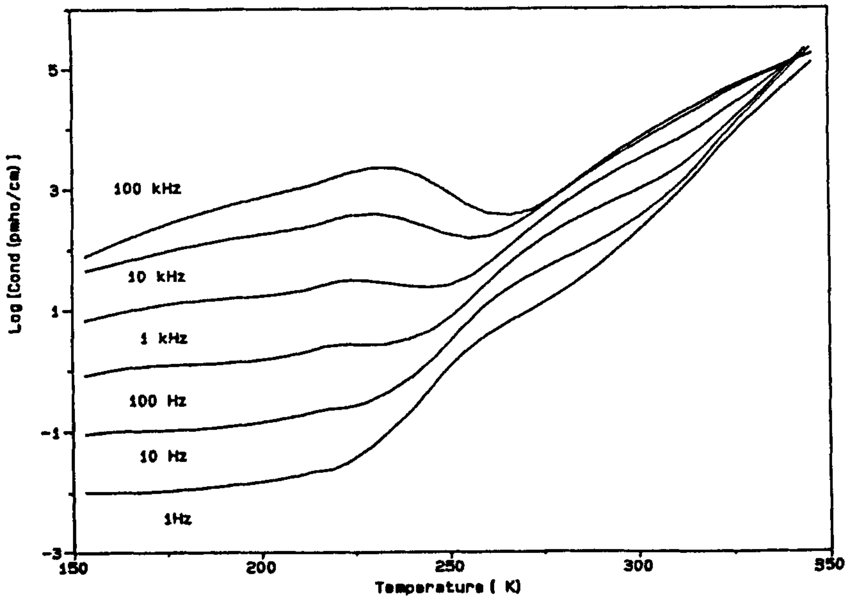

FIGURE 1 Conductivity vs. temperature of n-PEO at frequencies from 1 to 10^5 Hz.

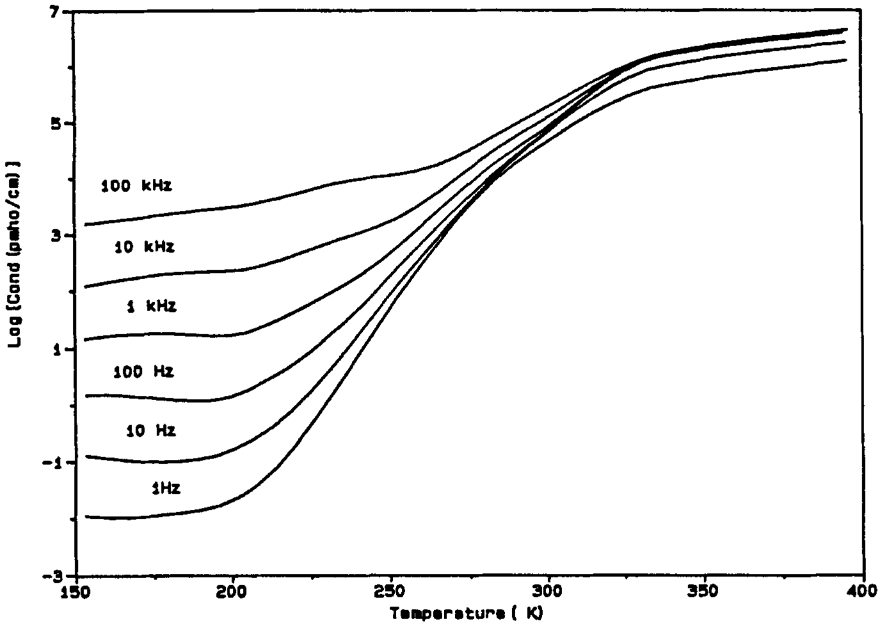

FIGURE 2 Conductivity vs. temperature of γ-PEO at frequencies from 1 to 10^5 Hz.

Figure 3 shows the behaviour vs. temperature of tan δ (the ratio between imaginary and real part of the complex dielectric constant, ε^*) at 1, 10 and 100 Hz, for γ-PEO (continuous lines) and n-PEO (dashed lines). The γ-PEO plots are characterized by two activated phenomena: the low-temperature broad peak (under the T_g) has been attributed [11] to the so-called γ-relaxation, that reflects the "local" motion of small segments of the polymer; the other large peak near the room temperature (α-relaxation) is referred to large scale segmental motions, associated with the glass transition. It is clear that γ-irradiation does not strongly affect the low-temperature phenomenon; on the contrary, the exposure causes the shoulder near the room temperature, well evident in Fig. 2, to disappear. Now, it is generally accepted that pure n-PEO contains both an amorphous and a crystalline phase and that the conductivity is primarily due to the amorphous one. On the other hand, it has been shown that the growth of the crystalline phase can be suppressed, or hindered, by incorporating irregularly spaced units [12] or cross-links [4] into the PEO chain, so the activated feature in the n-PEO tan δ may be tentatively assigned to a (partial) crystallization process. On this basis it is possible to explain the behaviour of log(σ) in Fig. 1: above the T_g the total conductivity is the sum of a "liquid-like" contribution (given by the amorphous phase) and of a frequency-dependent part connected to dipolar reorientation, that disappears above the melting point (~350 K) of the crystalline phase.

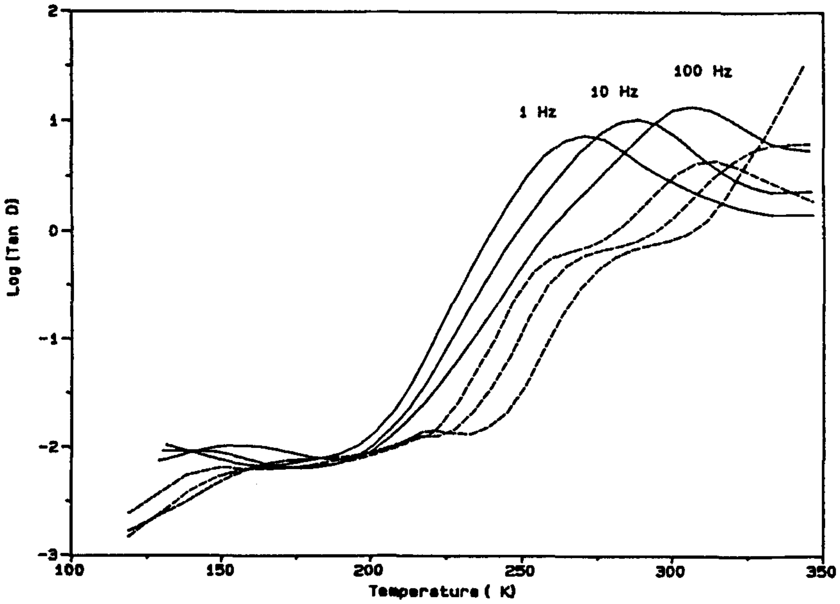

FIGURE 3 Comparison at various frequencies (1, 10, 100 Hz) of the behaviour of tan δ vs. temperature for γ-PEO (continuous lines) and n-PEO (dashed lines).

Figure 4 shows, for all the samples reported in Table I, the low-temperature region of tan δ (at 1 kHz) which contains the γ-relaxation peak. Let's compare, first of all, the effect of the γ-irradiation: the results on pure PEO are the enhancement of the dielectric loss and a slight shift of the relaxation peak to low temperature (see curve 1 vs. curve 4). However, no trend is evident for the PEO_n-$LiClO_4$ films; is it worthwhile to observe that γ-PEO_8-$LiClO_4$ (dotted line) does not exhibit a resonance and has a loss much higher than that of the other ones.

As far as salt-doped n-PEO is concerned, the addition of $Pb(ClO_4)_2$ causes an upward shift of the order of 10-15 K and an enhancement of the peak, as already observed for other systems [13], while the addition of $LiBF_4$ depresses the overall dielectric loss, and reduces the height of the peak. Our data seem to confirm the evidence of the interaction of the anion with the polymer chain, as already stated by Wintersgill and Fontanella [11].

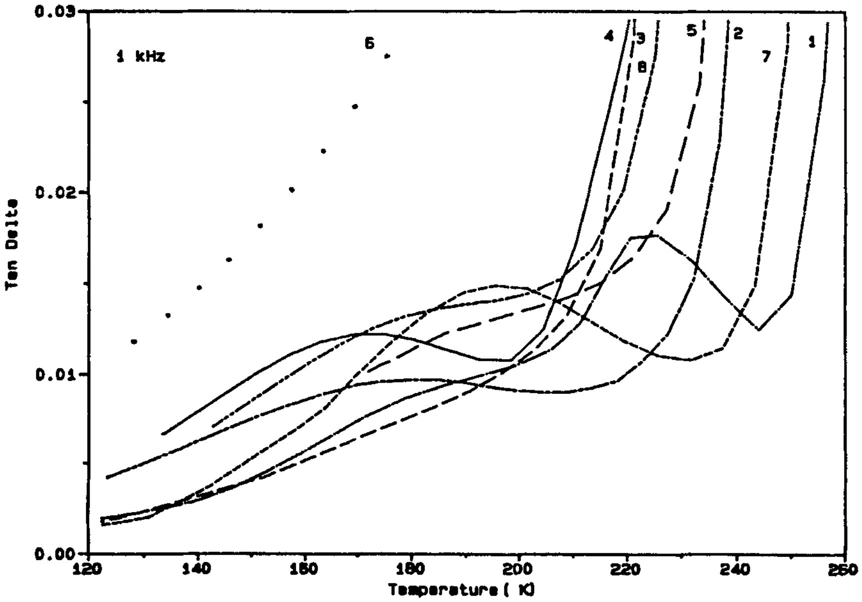

FIGURE 4 Behaviour of tan δ vs. temperature (at low temperature) for the samples studied. For the ID numbers refer to the Table I.

Finally, Table I resumes T_g and electrical data for the samples studied. The T_g values have been determined with the onset method both on tan δ and conductivity curves at 1 Hz; the values obtained from the two curves are consistent. The value obtained for n-PEO is fully consistent with previously reported thermal data [4], whereas the T_g of the other samples, both normal and irradiated, are substantially lower than our thermal values [4-6-7-8]. In addition, γ-irradiation seems to determine a lowering of the T_g. The values of permittivity and conductivity, on the contrary, are consistent with those reported in literature.

TABLE I Some electrical data of the samples studied.

#	Composition	T_g (K) (1 Hz)	ε'_{173} (100 kHz)	σ_{273} ($\Omega^{-1}cm^{-1}$) (100 kHz)	σ_{298} ($\Omega^{-1}cm^{-1}$) (100 kHz)
1	n-PEO	214	2.77	$1.92x10^{-10}$	$5.47x10^{-9}$
2	n-PEO_{20}-$LiClO_4$	231	2.72	$9.24x10^{-8}$	$1.24x10^{-6}$
3	n-PEO_8-$LiClO_4$	226	2.15	$2.49x10^{-7}$	$5.42x10^{-6}$
4	γ-PEO	204	2.56	$2.95x10^{-8}$	$1.77x10^{-7}$
5	γ-PEO_{20}-$LiClO_4$	230	2.45	$3.11x10^{-7}$	$5.13x10^{-6}$
6	γ-PEO_8-$LiClO_4$	205	4.83	$1.17x10^{-5}$	$6.72x10^{-5}$
7	n-PEO_{20}-$Pb(ClO_4)_2$	240	3.49	$2.85x10^{-8}$	$2.98x10^{-7}$
8	n-PEO_{20}-$LiBF_4$	215	3.15	$8.52x10^{-7}$	$5.90x10^{-6}$

CONCLUSIONS

The DR analysis technique is able to yield an important insight both into the structural properties and into the ionic transport phenomena occurring in polymer-based solid electrolytes. In particular, this work confirms that γ-irradiated (cross-linked) PEO-based polymers have amorphous phases more stable than the not-irradiated ones and that their room-temperature conductivity is greater than that of the normal ones. Above the glass transition temperature, in addition, the conductivity of the irradiated films is almost entirely determined by a transport mechanism, while the not-irradiated polymers are dominated at low frequencies by a strong dipolar effect.

The cross-linking procedure slightly affects the γ-relaxation, usually assigned to local motions of pieces of the polymers chains; on the other hand, this relaxation is confirmed to be a good probe in monitoring the interactions between the added salts and the skeleton of the polymer.

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