



Ionic, paramagnetic and photophysical properties of a new biohybrid material incorporating copper perchlorate



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ABSTRACT

The sol-gel method was employed in the synthesis of di-urethane cross-linked poly(ϵ -caprolactone) (d-PCL(530)/siloxane biohybrid ormolytes incorporating copper perchlorate ($\text{Cu}(\text{ClO}_4)_2$). The highest ionic conductivity of the d-PCL(530)/siloxane_n $\text{Cu}(\text{ClO}_4)_2$ system is that with $n=10$ (1.4×10^{-7} and $1.4 \times 10^{-5} \text{ S cm}^{-1}$, at 25 and 100 °C, respectively). In an attempt to understand the ionic conductivity/ionic association relationship, we decided to inspect the chemical environment experienced by the Cu^{2+} ions in the d-PCL(530)/siloxane medium. The observed EPR spectra are typical of isolated monomeric Cu^{2+} ions in axially distorted sites. The molecular orbital coefficients obtained from the EPR spin Hamiltonian parameters and the optical absorption band suggests that bonding between the Cu^{2+} and its ligand in the ormolytes are moderately ionic. Investigation by photoluminescence spectroscopy did not evidence or allow selective excitation of transitions corresponding to complexed Cu^{2+} species.

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1. Introduction

Polymer electrolytes (PEs) are potentially interesting as electrolytes for solid-state electrochemical devices [1,2]. It is also recognized that the most important properties of solid electrolyte solutions are non-volatility and moderate ionic conductivity. The most extensively studied host polymer has been poly(oxyethylene) (PEO), a hard polybasic macromolecule, which exhibits an extraordinary capacity to solvate ionic salts. However, PEO has major disadvantages that have severely restricted practical applications such as a marked tendency to crystallize or that at high salt concentration the solubility limit is exceeded and salting-out is often observed. Under these circumstances the mechanical properties of these materials are rather poor. Among the strategies that have been proposed to overcome these drawbacks the combination of the sol-gel method [3] with the hybrid concept [4] and the development of modified electrolytes is considered to be a very attractive approach. The versatility provided by the sol-gel method has attracted growing interest, within the material science community, for the preparation of advanced organic-

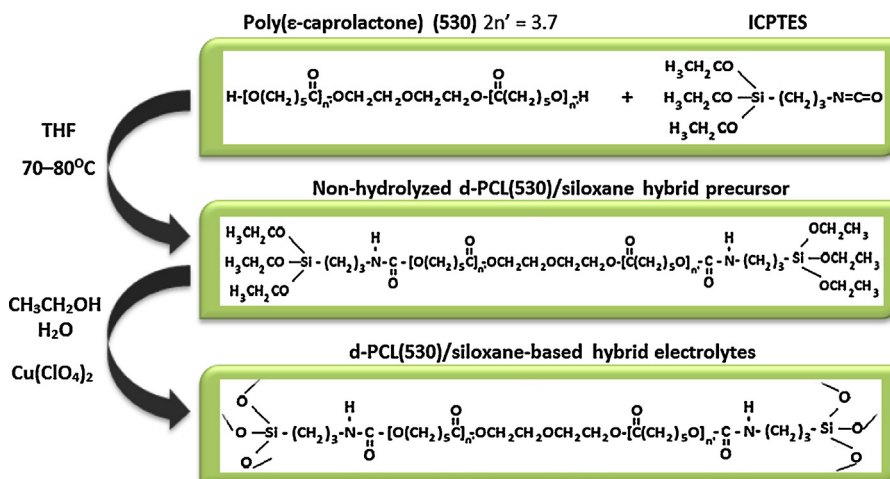
inorganic hybrid materials with potential application in several technologically important domains including solid-state electrochemistry, optics, electronics, biology and medicine [5–16].

From the research carried out in this field, a series of attractive sol-gel-derived “low environmental impact” electrolytes have been developed based on the di-urethane cross-linked d-PCL(530)/siloxane network (where d represents di, PCL identifies the poly(ϵ -caprolactone) biopolymer, and 530 is the average molecular weight in grams per mole). The resulting hybrid materials are essentially amorphous, and typically these materials exhibit good processability, high thermal, mechanical and chemical stability, and they are able to solubilize significantly higher guest salt concentrations than conventional PEs.

The d-PCL(530) / siloxane matrix provides three types of donor atoms: (1) the carbonyl oxygen atoms of urethane cross-links; (2) the ester carbonyl oxygen atoms of the PCL(530) chains and (3) the ether oxygen atom of the PCL(530) central oxyethylene segment. The incorporation of increasing amounts of the guest salts leads to a strengthening of the hydrogen bonds, a saturation of the urethane free C=O groups and a formation of new and very strong cation-coordinated hydrogen – bonded aggregates. To investigate the chemical surrounding of various C=O environments present in the d-PCL(530)/siloxane hybrids and elucidate the relationship between ionic conductivity and ionic association/local

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coordination, Electron Paramagnetic Resonance (EPR) spectroscopic analyses were performed on some of these hybrid electrolytes.

Electron Paramagnetic Resonance (EPR) is a sensitive spectroscopic technique for the study of a local coordination environment of paramagnetic centers such as transition metals, incorporated in a variety of materials [17]. Copper is a transition metal of importance in many catalytic and biological systems and EPR spectroscopy is particularly suitable for the study of the nature and magnetic properties of Cu^{2+} doped polymer electrolytes and biomembranes [18–20]. Furthermore, because the host-ion combination could also lead to interesting luminescent properties, potentially useful in multifunctional devices, the photophysical characterization is justified.

The present study is devoted to the ionic and spectroscopic characterization of the d-PCL(530)/siloxane systems doped with $\text{Cu}(\text{ClO}_4)_2$ for which no information exists at present, to the best of our knowledge.

2. Experimental

2.1. Synthesis

Copper perchlorate ($\text{Cu}(\text{ClO}_4)_2$, Aldrich), was dried under vacuum at 25°C for several days prior to being used. α,ω -hydroxypoly(ϵ -caprolactone) (PCL (530), Fluka, average molecular weight = 530 g mol^{-1}) and 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich, 95%) were used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity water (H_2O) was used in all experiments.

The d-PCL(530)/siloxane-based hybrid electrolytes were prepared (Scheme 1) according to the procedure described in detail elsewhere [21]. In the first step a urethane cross-link was formed between the hydroxyl (-OH) end groups of PCL(530) (0.80 g, 1.51 mmol) and the isocyanate (-N=C=O) groups of ICPTES (745 μL , 3.01 mmol) in THF at $70\text{--}80^\circ\text{C}$ resulting in a non-hydrolysed hybrid

precursor. In the second step $\text{CH}_3\text{CH}_2\text{OH}$ (705 μL , 12.07 mmol) and water (82 μL , 4.55 mmol) were added to this solution to promote a characteristic sol-gel reactions i.e., hydrolysis and condensation. The salt of $\text{Cu}(\text{ClO}_4)_2$ was incorporated in the latter stage in the quantities depicted in Table 1. The ormolyte sample, produced as a xerogel film, was aged for 1 month in an oven at 50°C followed by an under vacuum final drying at 90°C for 3 days prior to being analysed. The series of materials were identified by the notation d-PCL(530)/siloxane $_n\text{Cu}(\text{ClO}_4)_2$, where n corresponds to the number of $\text{C}(=\text{O})(\text{CH}_2)_5-\text{O}-$ repeat units of PCL(530) per Cu^{2+} ion. The PCL-copper perchlorate solvent-free polymer electrolytes prepared in this study presented themselves in the form of flexible membranes (Fig. 1).

2.2. Characterization Techniques

The total ionic conductivity of the samples was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, > 99.95%) to form a symmetrical cell. The electrode/polymer electrolyte/electrode assembly was secured in a suitable constant volume support and installed in a Büchi TO51 tube oven with a K-type thermocouple placed close to the electrolyte disk to measure the sample temperature. Bulk conductivities of the electrolyte samples were obtained during heating cycles using the complex plane impedance technique using the Autolab PGSTAT-12 (Eco

Table 1
Quantities of $\text{Cu}(\text{ClO}_4)_2$ salt added to each sample.

n	m ($\text{Cu}(\text{ClO}_4)_2$) (g)	n ($\text{Cu}(\text{ClO}_4)_2$) (mmol)
5	0.29	1.12
8	0.18	0.70
10	0.15	0.56
20	0.07	0.28



Fig. 1. Photograph of representative $\text{PCL}_n\text{Cu}(\text{ClO}_4)_2$ sample.

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