



Synthesis, CO₂ sorption and capacitive properties of novel protic poly(ionic liquid)s



Paola Cardiano^{a,*}, Olivia Gómez-Laserna^b, Placido G. Mineo^{c,d}, Emilia Furia^e, Claudia Triolo^f, Salvatore Patanè^f, Sandra Lo Schiavo^a

^a Dipartimento Di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

^b Departamento de Química Analítica, Universidad del País Vasco (EHU/UPV), Barrio Sarriena s/n, E-48080, Leioa, Bilbao, Spain

^c Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria 6, 95125 Catania, Italy

^d CNR-IPCB Istituto per i Polimeri, Compositi e Biomateriali, Via P. Gaifami 18, 95126 Catania, Italy

^e Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, Cubo 12/D, 87036 Arcavacata di Rende, Cosenza, Italy

^f Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

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ABSTRACT

A series of poly(ionic liquid)s based on the protic monomers obtained by the straight acid-base reaction between the polymerizable 2-(methacryloyloxy)ethyl-phthalic acid and trihexylamine, trioctylamine and dicyclohexylamine have been synthesized and characterized. The assessment of their macromolecular nature is based on FT-IR and ¹H NMR spectroscopy, viscosimetry and MALDI-TOF mass spectrometry. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG-DTA) reveal the amorphous behavior of the new poly(ionic liquid)s with a glass transition temperature ranging from ca. 2 to 67 °C and a relatively low thermal stability attributed to the decarboxylation of polyanions. Dynamic contact angles data are consistent with a hydrophilic behavior. Quartz Crystal Microbalance investigations display a fast, reversible and linear response towards CO₂, being the dicyclohexylamine-based poly(ionic liquid) the most performing one. Electrochemical impedance spectroscopy investigations on trihexylamine poly(ionic liquid) are also reported.

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1. Introduction

Ionic liquids (ILs) are salts, solely composed of ions, having melting points below 100 °C. They are made of organic cations and organic or inorganic anions whose asymmetry generally inhibits packing and thus crystallisation. These features infer them a large variety of appealing properties such as non-volatility, non-flammability, unique thermal and chemical stability, wide electrochemical window etc. [1]. Most attractiveness of ILs arises from the possibility to be properly “engineered” for specific applications by an accurate selection of cation/anion couple. This explains why this unique class of electrolytes had a high impact in many fields, beside the conventional use as simple and active solvents in synthetic and catalytic industrial processes [2–4]. More recently, the attention has been focused on the so-called “supported ILs”, i.e. ILs materials featured by ILs units on proper substrates such as nano-scaffolds or polymeric networks, which can exhibit enhanced properties and new functions.

Among other classifications, ILs may be distinguished into two main categories: aprotic (AILs) and protic ionic liquids (PILs). The latter,

which are easily obtained by the proton transfer from Brønsted acids to Brønsted bases, although initially less investigated than AILs, emerged as a new class of proton-conducting electrolytes with applications in aqueous batteries, fuel cells, double layer capacitors, actuators, dye-sensitized solar cells, propellant or explosive [5–7]. Their intrinsic capability to promote hydrogen bonds was, likewise, exploited in designing self-assembly networks [8,9]. Analogously to AILs, PILs based on ammonium cations have been investigated as functional materials in the context of separation science, especially in chromatography [10, 11] displaying a high selectivity towards solutes that are polar and/or hydrogen donors or acceptors [5]. The presence of anions with a strong and tunable basic character makes, on the other hand, this class of ILs a good candidate for the “absorption” of acidic molecules. Accordingly, many studies are now available confirming not only their peculiar sorption properties towards acidic gases such as CO₂ and SO₂ [12,13], but they also point out the potential of PILs to act as specific adsorbents. Mattedi et al., for example, have found that protic ionic liquid *N*-methyl-2-hydroxyethylammonium acetate can be exploited to selectively separate carbon dioxide from methane mixture also at low CO₂ molar concentration [14]. Besides, Xing-Bang Hu et al. reported on supported liquid membranes impregnated with mono- and di-carboxylate ammonium PILs which facilitated the separation of CO₂ and SO₂ [15]. It is also

* Corresponding author.

E-mail address: pcardiano@unime.it (P. Cardiano).

to underline that being carboxylic acids widespread in nature, a large variety of monomeric and polymeric PILs may be designed starting from natural and renewable sources [16].

In the context of our previous works aimed at exploring the potential applications of ILs-based materials [17–22], we have reported also on two series of polymerized ionic liquids (poly(IL)s, i.e. polymers deriving from the polymerization of monomeric ILs) based on the 1-vinyl-3-hexylimidazolium and [2-(methacryloyloxy)ethyl]dimethylheptyl ammonium cations, respectively, and a variety of anions which exhibit a fast and reversible CO₂ response with a sensitivity performance dependent, in some extent, on the nature of the anions [23,24].

As a continuation of our ongoing research on CO₂ sorption capabilities of discrete and polymeric ILs, we turned our attention on the CO₂ sorption properties of protic polyanionic-based ILs. In particular, we report on the synthesis of new monomeric ammonium-based protic ionic liquids obtained by neutralization of trihexylamine, trioctylamine and dicyclohexylamine by a polymerizable Brønsted acid, namely 2-(methacryloyloxy)ethyl-phthalic acid, and on the polymerization of the as prepared ammonium salts. All the new compounds have been characterized by means of ¹H NMR and FT-IR spectroscopy; their thermal properties have been established by DSC and TG-DTA investigations. The macromolecular nature of the poly(ionic liquid)s has been ascertained by MALDI-TOF mass spectrometry and viscosimetric measurements. Poly(ionic liquid)s hydrophobic and CO₂ sorption/desorption properties at room temperature have been established as well. The capacitive behavior of the trihexylamine poly(ionic liquid) film was also explored by electrochemical impedance spectroscopy (EIS) using a cell featured by a ITO/poly(IL)/Al sandwich structure [25].

2. Experimental section

2.1. Materials

Trihexylamine, trioctylamine, dicyclohexylamine and 2-(methacryloyloxy)ethyl-phthalic acid were purchased from Sigma Aldrich and used as received.

2.2. Measurements

¹H NMR solution spectra were carried out with a Bruker AMX R-300 spectrometer operating at 300.13 MHz. FT-IR spectra were obtained on KBr disks by using a Perkin-Elmer Spectrum BX spectrometer. Thermogravimetric investigations were performed by means of Perkin-Elmer Pyris TGA7 in the temperature range between 50 and 800 °C, under nitrogen flow (60 mL min⁻¹) and heating rate of 10 °C min⁻¹. Differential scanning calorimetry measurements were carried out by using a TA Q20 instrument equipped with a Refrigerant Cooling System (RCS) with a heating rate of 10 °C min⁻¹, under an anhydrous N₂ atmosphere (60 mL min⁻¹). The cooling rates were fixed at 50 °C min⁻¹. For the determination of the protonation constants, MTHA, MTOA and MDCHA stock solutions were prepared by using methanol as solvent. Potentiometric measurements were performed by using a cell arrangement analogous to the one described by Forsling et al. [26] and the reference electrode was prepared according to Brown [27]. The titrations were carried out as described in a previous paper [28]. A slow stream of nitrogen gas was passed through the gas inlet tube into the test solutions stirred during titrations after the passage through four bottles (a–d) containing: a) 1 M NaOH, b) 1 M H₂SO₄, c) twice distilled water, and d) 1 M NaClO₄. The cell assembly was retained in a thermostat kept at (25.0 ± 0.1) °C. The perchloric acid stock solution and the sodium hydroxide titrant solutions were prepared and standardized as described in a previous work [29]. A sodium perchlorate stock solution was prepared and standardized according to Biedermann [30]. The protonation constants, *K*_a, of MTHA, MTOA and MDCHA, were evaluated at 25 °C and in 1 M NaClO₄.

All the measurements were performed as potentiometric titrations with an alkaline glass electrode, GE, with cell (G) Reference Electrode / Test Solution / GE (G).

Test solution had the general composition: C_L M ILs, C_A M HClO₄, C_B M NaOH, (1 – C_A – C_B) M Na⁺, where C_L were varied between (0.55 · 10⁻³ and 1.10 · 10⁻³) M and the pH range was 8.5–11.5. The primary C_L, C_A, C_B and [H⁺] data form the basis of the treatment to obtain the protonation constants. The positive MALDI-TOF mass spectra were collected by a Voyager DE (PerSeptive Biosystem) using a delay extraction procedure (25 kV applied after 2600 ns with a potential gradient of 454 V mm⁻¹ and a wire voltage of 25 V) [31,32] with ion detection in linear mode. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2). In order to avoid fragmentation of the polymers, the laser irradiance was maintained slightly above threshold (approx. 10⁶ W cm⁻²). Each spectrum was an average of 32 laser shots. The MALDI investigations were performed by loading on the plate a 0.1 mmol sample and 40 mmol matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB), with DMF as solvent. Both 5,10-di(*p*-dodecanoxyphenyl)-15,20-di(*p*-hydroxyphenyl) porphyrin (C₆₈H₇₈N₄O₄, 1014 Da), tetrakis(*p*-dodecanoxyphenyl)porphyrin (C₉₂H₁₂₆N₄O₄, 1350 Da) and a PEG sample of known structure were used as external standards for *m/z* calibration [33–35]. Inherent viscosities of the polymers ($\eta_{inh} = \ln \eta_r/c$; *c* = 0.5 g dL⁻¹) were measured in a Desreux-Bischoff suspended level viscometer, in DMF at 30 °C. Since the polymers are insoluble in solvents compatible with our GPC columns set, the evaluation of the averages molecular masses and distribution of the polymers could not be performed. Dynamic contact angle measurements were performed on coated glass microscopy slides (26 × 76 × 1 mm by Prestige) using the Wilhelmy method by means of a KSV Sigma 700 tensiometer at a speed of 2 mm min⁻¹ in ultrapure water. Before use, the glass slides were carefully cleaned by sulfuric acid-k-dichromate cleaning solution, then washed with ultrapure water and checked by measuring the surface tension of water. Then the slides were dip-coated by immersion-withdrawn cycles into 7.5 wt% methanol solution (for PDCHA, see below) and acetone solutions (for PTHA and PTOA) at a constant rate of 20 mm min⁻¹, without any delay between immersion and withdrawn. After being dip-coated, the slides were aged for 10 days at 50 °C, and then contact angle measurements were carried out. The reported contact angle values are the average of the measurements performed on five different glass slides treated in the same way. Furthermore, in order to observe the wetting effect due to water on samples surfaces, five continuous immersion-withdrawn cycles have been performed on each coated slide. Quartz crystal microbalance measurements have been carried out on 20 MHz AT-cut piezoelectric quartz crystals (PQCs) with 5 mm diameter gold electrodes by means of Bioage Eureka QCM equipped with a flow-through chamber for gases. The balance mass sensitivity was 0.4 ng Hz⁻¹. The deposition of the polymeric films, on both sides of PQCs, has been achieved by drop casting. In order to gain a suitable piezoelectric response (i.e. fast and reproducible with good signal/noise ratio), several deposition attempts by varying the solution concentration of each polymer have been carried out. Accordingly, 1 μL of methanol solutions of poly(IL)s (ca. 5 mg mL⁻¹) have been deposited onto the gold electrode with a Hamilton GC syringe. Once methanol evaporated, the behavior of poly(IL)s towards CO₂ has been investigated exposing the coated PQCs to a flow of N₂ (i.e. carrier gas) and CO₂, at room temperature, by varying CO₂ percentages. Relative amounts of the two gases have been selected by two mass flow controllers, with a fixed total gas flux (300 mL min⁻¹) conveyed to the measurement cell. More in detail, each coated PQC has been placed into the detection chamber and allowed to equilibrate under N₂ flow up to the frequency metric signal stability. The frequency variations of each coated crystal were measured as a function of time

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