



Editor's choice paper

## Ionic liquids/ZnO nanoparticles as recyclable catalyst for polycarbonate depolymerization



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### ABSTRACT

A useful protocol for waste bis-phenol A-polycarbonates (BPA-PC) chemical recycling is proposed based on a bifunctional acid/basic catalyst composed by nanostructured zinc oxide and tetrabutylammonium chloride (ZnO-NPs/NBu<sub>4</sub>Cl) in quality of Lewis acid and base, respectively. Retro-polymerization reaction proved to be of general application for several nucleophiles, including water, alcohols, amines, polyols, aminols and polyamines, leading to the complete recovery of BPA monomer and enabling the PC polymer to function as a green carbonylating agent (green phosgene alternative) for preparing carbonates, urethanes and ureas. A complete depolymerization can be obtained in seven hours at 100 °C and ZnO nanocatalyst can be recycled several times without sensible loss of activity. Remarkably, when polycarbonate is reacted with glycerol, it is possible to realize in a single process the conversion of two industrial wastes (BPA-PC and glycerol) into two valuable chemicals like BPA monomer and glycerol carbonate (the latter being a useful industrial solvent and fuel additive).

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### 1. Introduction

Growing of plastic wastes, together with CO<sub>2</sub> emission, is another plague of modernity. The increasing level of plastic wastes in the environment is an urgent problem that needs fast responses. Actually, politics and researchers are pursuing two different strategies to reduce plastic dispersal: i) recycling of plastic items, and ii) incineration of plastic wastes [1]. However, in this latter case, a further drawback has to be considered, connected to the identification of suitable storage sites and to the minimization of the risk of the industrial plants. For these reasons, in the last years, the chemical valorisation of plastic wastes is regaining more and more interest as a complementary way to the thermovalorisation. In fact, some plastics can be considered as a source of CO<sub>2</sub> that can be introduced, as chemical synthon, in important and valuable products such as carbamates, urethanes and heterocyclic structures, just to cite a few [2]. For example, carbon dioxide is also present into an important and widespread polymer such as bis-phenol A polycarbonates (BPA-PC), a thermoplastic material with significant properties as

good stability, excellent flexibility and good transparency [3]. BPA-PC recycling is often difficult, then incineration becomes an easy way to produce electricity and to avoid landfills disposal. However, pyrolysis of BPA-PC results in the release of a large amount of greenhouse gases released and low-value carbonaceous products.

Alternatively, chemical depolymerization has to be considered the most promising technique for recycling waste polymers and plastics. Chemical polymer degradation can represent a potential option for converting plastics into their monomers or other valuable products (depolymerization) [4]. Alcoholysis, aminolysis and hydrolysis [5] are conventional procedures typically performed at high pressure and temperatures as well as in the presence of large quantities of concentrated acids or bases during long time processing [6].

Among these methods, depolymerization of BPA-PC has been done by using hot compressed water [7], alkaline solutions [8], supercritical ethanol [9], microwave irradiation [10], and metal catalysts such as Mn(OAc)<sub>2</sub> [7] and a variety of metal oxides and salts [11,12].

Recently, besides the chemical recovery of the starting monomer (BPA), particularly attractive became the use of polycarbonate as carbonylating agent in an economic and environmentally benign non-phosgene alternative for preparation of many car-

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bonyl derivatives (carbonates, carbamates, etc.). As an example, methanolysis of polycarbonate can lead simultaneously to the recovery of the starting monomer BPA and to the synthesis of dimethylcarbonate (DMC), an industrially important solvent and methylating agent.

During the past decades, we have been focusing our efforts in developing powerful catalytic methods using ionic liquid (ILs) as both catalysts and reaction media [13]. In particular, we paid attention to tetraalkylammonium salts that are capable of stabilizing metal nanoparticles providing them a protecting shell that impedes aggregation, thus prolonging catalyst lifetime and facilitating its prompt recycling. In addition, due to the shielded positive charge on cationic nitrogen, tetraalkylammonium salts anions are good nucleophiles and can behave as basic catalysts themselves.

Based on our skills in handling metal nanocatalysts [14], and being PC transesterification also promoted by a variety of Lewis acids, we decided to conjugate the nucleophilic/stabilizing ability of quaternary tetraalkylammonium ILs with the Lewis acid properties of ZnO, a catalyst successfully employed in depolymerization processes (e.g. on polyethylene terephthalate) [15], developing an efficient and recyclable bifunctional  $\text{NBu}_4\text{Cl}/\text{ZnO}$ -NPs catalyst useful for depolymerization of polycarbonate waste material. In this study, ZnO nanoparticles (ZnO-NPs) were synthesized by a hybrid electrochemical-thermal process [16] and the influence of calcination temperature on catalytic performance was evaluated.

## 2. Experimental

### 2.1. Materials and general procedure

Unless otherwise stated, all manipulations were carried out in air. Solvents, metal oxides, nucleophilic reactants (alcohols, amines, phenols, diols, glycerol, diamines and aminols) and additives ( $\text{BuNH}_2$ , pyridine, ILs), were Aldrich or Fluka products and were used as received. Bisphenol A-Polycarbonate (BPA-PC) with an average molecular mass of 45,000 was purchased by Sigma-Aldrich.

Reaction products were identified by IR, GLC-MS and  $^1\text{H}$  NMR, by comparison with the literature data or with authentic samples (spectral data are reported into the Supplementary material). IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrophotometer. GLC-MS analyses were carried out with a Shimadzu GLC 17-A linked to a Shimadzu GLC/MS QP5050A selective mass detector (capillary column: HP-5 MS, 30 m).

Depolymerization percentages were determined measuring the ratios of the chromatographic areas between the BPA and the end capping agent 4-(2-phenylpropan-2-yl)phenol released by the polymer (BPA-PC from Sigma-Aldrich) during the reaction, according to a procedure described into the Supplementary material.

Catalytic tests were carried out in a 55.6 mL stainless steel autoclave mounted in an electrical oven having a magnetic stirrer on its base. Catalysts, solvent and reagents were introduced in a glass vial (~12 mL) placed into the autoclave, in order to avoid any contact with metal walls.

### 2.2. Preparation of ZnO nanoparticles catalysts

A three-electrode conventional cell was employed to perform the electrochemical synthesis: highly pure zinc sheets (Goodfellow, 99.99+%) were used as working and counter electrodes, while an  $\text{Ag}/\text{AgCl}$  (in saturated KCl) was the reference electrode. Electrolytic solution consisted of 1 g/L PSS [Poly(sodium-4-styrenesulfonate, average Mw ~ 70,000, Sigma) in 30 mM  $\text{NaHCO}_3$  (purum p.a.,  $\geq 99.0\%$ ). Electrodes were polished with alumina (Sigma) and sonicated in Milli-Q water before use. Zinc activation in 1 M HCl (Fluka) was performed for 30 s just before immersion

in the electrolytic bath. Afterwards, the electrosynthesis was carried out under galvanostatic conditions ( $j = 10 \text{ mA}/\text{cm}^2$ ) for 1 h at room temperature under stirring, using a CH-1140b potentiostat-galvanostat (CH Instruments, USA). The resulting nanocolloid was then collected and centrifuged at 5000 rpm for 45 min. The obtained precipitate was dried at  $70^\circ\text{C}$  in an oven overnight. Finally, the thermal annealing step for the synthesis of ZnO-NPs was performed either at  $300^\circ\text{C}$  or at  $600^\circ\text{C}$  for 1 h.

TEM characterization was performed with a FEI Tecnai 12 instrument (HV: 120 kV; LaB6 filament) on aqueous suspensions of calcined ZnO-NPs using Formvar<sup>®</sup>-coated Cu s (300 mesh, Agar Scientific).

XPS analysis was carried out using a Theta Probe Spectrometer equipped with  $\text{AlK}\alpha$  source and beam spot diameter of  $300 \mu\text{m}$ . All XPS and Auger spectra were registered in constant analyzer energy (CAE) mode. Survey scans were registered at a pass energy of 150 eV and step size 1.0 eV. Besides, high-resolution spectra (C1s, O1s, Zn2p,  $\text{ZnL}_3\text{M}_{45}\text{M}_{45}$ , S2p and Na1s) were acquired at 100 eV with 0.1 eV step size.

XPS quantification was performed with Thermo Advantage software (v. 4.75, © 1999–2010 Thermo Fisher Scientific). A Shirley background removal and a database of Scofield sensitivity factors optimized for oxides were used for processing. Signal positions were corrected on the basis of C1s aliphatic component set at 284.8 eV.

FTIR spectra on commercial ZnO (Sigma) and calcined nanopowders were collected on a BioRad FTS6000 instrument in the 4000–400  $\text{cm}^{-1}$  range (resolution 4  $\text{cm}^{-1}$ ) preparing KBr pellets.

### 2.3. Catalytic tests

In a typical experiment, a 50 mL glass vial was charged with THF (5 mL) and 1 mmol of BPA-Polycarbonate that was left to dissolve under vigorous stirring for 10 min at room temperature. Then, ZnO-NPs,  $\text{Bu}_4\text{NCl}$  and nucleophile reagent were added and the vial introduced into the autoclave, which was sealed and charged with  $\text{N}_2$  at atmospheric pressure. The autoclave was heated at  $100^\circ\text{C}$  for the proper reaction time.

Next, it was cooled to room temperature, then centrifuged to remove ZnO nanoparticles and then analyzed by IR and GC-MS for reactants and products. Procedure for isolation of reaction products was dependent on the nucleophiles employed for depolymerization (water, alcohols or amines).

In the case of hydrolysis, procedure was more simple, being BPA the sole reaction product (apart carbonic acid). To isolate BPA starting monomer, reaction mixture was treated with aqueous HCl under vigorous stirring and extracted more times with  $\text{Et}_2\text{O}$ . The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. Recrystallization of the residue from chloroform and hexane gave highly pure bisphenol A.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.75 (s, 6H), 7.13–7.15 (d, 4H), 7.22–7.24 (d, 4H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  31, 43, 120, 128, 148, 152, GC-MS  $m/z$  (%): 228 ( $\text{M}^+$ , 27), 213 (100), 119 (64), 43 (26), 99 (10), 91 (12), 65 (6) [17].

In the case of alcoholysis and aminolysis, procedures were complicated by the separation of BPA from the carbonylated products (carbonates, urethanes and ureas). Procedures are reported into the Supplementary material together with spectral data used for identification.

### 2.4. Procedure for catalyst recycling

Recycling experiments were checked on hydrolysis as model reaction. A 50 mL glass vial was charged with THF (5 mL) and 1 mmol of BPA-Polycarbonate that was left to dissolve under vigorous stirring for 10 min at room temperature. Then, ZnO-NPs,  $\text{Bu}_4\text{NCl}$  (5 mol%) and water (30 mmol) were added and the vial introduced

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