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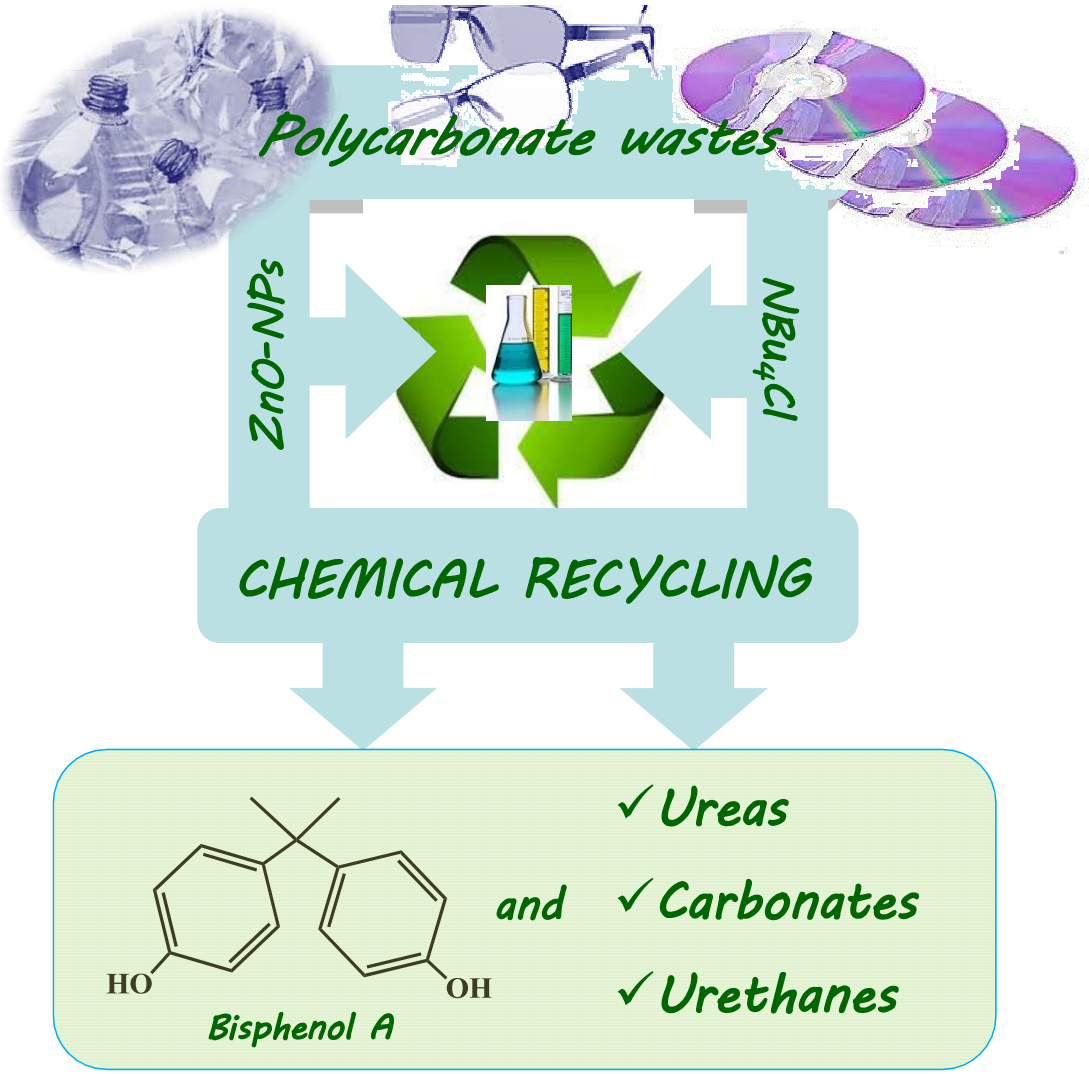
*Graphical Abstract



Highlights

►$ZnO_{nanop.}$/NBu_4Cl act as an highly efficient bifunctional catalyst for retro-polymerization of bis phenol A – polycarbonate (BPA-PC)

►Protocol is of general application for several nucleophiles, including water, alcohols, amines, polyols, aminols and polyamines

►BPA-PC behaves as an economic and environmentally benign non-phosgene alternative for the preparation of carbonates, urethanes and ureas

►The simultaneous valorization of two industrial wastes like BPA-PC and glycerol is possible

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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 ($ZnO_{nanop.}$/NBu_4Cl) 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).

Keywords: ionic liquids; zinc oxide nanoparticles; polycarbonate; depolymerization.

1. Introduction

Growing of plastic wastes, together with CO_2 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_2 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 $Mn(OAc)_2$ [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 carbonyl 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 catalysts 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 [13b].

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 successful employed in depolymerization processes (e.g. on polyethylene terepththalate) [15], developing an efficient and recyclable bifunctional $NBu_4Cl/ZnO_{nanop.}$ 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 ($BuNH_2$, 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}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 still 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 Ag/AgCl (in saturated KCl) was the reference electrode. Electrolytic solution consisted of 1 g/L PSS (average Mw ~ 70,000, Sigma) in 30 mM $NaHCO_3$ (purum p.a., ≥ 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 mA/cm2) 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 minutes. The obtained

precipitate was dried at 70°C in an oven overnight. Finally, the thermal annealing step for the synthesis of ZnO-NPs was performed either at 300°C or at 600°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®-coated Cu s (300 mesh, Agar Scientific).

XPS analysis was carried out using a Theta Probe Spectrometer equipped with AlKα source and beam spot diameter of 300 μm. 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, $ZnL_3M_{45}M_{45}$, S2p and Na1s) were acquired at 100 eV with 0.1 eV step size.

XPS quantification was performed with Thermo Avantage 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 cm-1 range (resolution 4 cm-1) preparing KBr pellets.

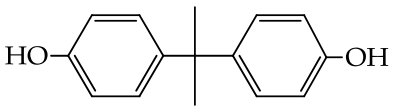
2.3. Catalytic tests

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 minutes at room temperature. Then, ZnO-NPs, Bu_4NCl and nucleophile reagent were added and the vial introduced into the autoclave, which was sealed and charged with N_2 at atmospheric pressure. The autoclave was heated at 100°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 Et_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. Recrystallization of the residue from chloroform and hexane gave highly pure bisphenol A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 6H), 7.13-7.15 (d, 4H), 7.22-7.24 (d, 4H); ^{13}C NMR (400 MHz,CDCl3), δ 31, 43, 120, 128, 148, 152, GC-MS m/z (%): 228 (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 minutes at room temperature. Then, ZnO-NPs, Bu_4NCl (5 mol%) and water (30 mmol) were added and the vial introduced into the autoclave, which was sealed and charged with N_2 at atmospheric pressure. The autoclave was heated at 100°C for 7 hours.

Being insoluble in THF, ZnO nanoparticles remained as precipitate at the end of the depolymerization process and were removed from the reaction medium by centrifugation, dried with a nitrogen stream and then promptly reused by adding fresh reagents and Bu_4NCl co-catalyst.

In this way, the Lewis acid catalyst ZnO nanoparticles could be recycled up to five cycles with negligible loss of activity (fig. 7), whereas its basic counterpart Bu_4NCl was only partially recovered with the following separation procedure. After centrifugation, reaction mixture was treated with aqueous HCl and extracted with ethyl ether. The organic layer was treated to recovery BPA, while aqueous solution was evaporated and the residue re-dissolved into chloroform, dried over Na_2SO4 and re-evaporated furnishing almost pure Bu_4NCl (yield 39%).

3. Results and discussion

3.1. Synthesis and characterization of ZnO nanocatalyst

ZnO-NPs were prepared according to a two-step process developed in our laboratory [16]. In the first step, jellified nanocolloids consisting of zinc hydroxide-carbonate were electrochemically synthesized under mild and green conditions, in the presence of an anionic stabilizer [poly(sodium-4-styrenesulfonate), PSS] in sodium bicarbonate aqueous solution. In place of zinc(II) salts used in hydrothermal methods, a sacrificial anode made of pure Zn (see experimental part) was employed as a source of Zn^{2+} ions. These process proved to have a very high yield (> 90%) and low power consumption. The electrochemical procedure allowed the formation of zinc mixed species of undefined morphology that were easily converted into spheroidal ZnO nanostructures by thermal treatment at temperatures above 250°C [16].

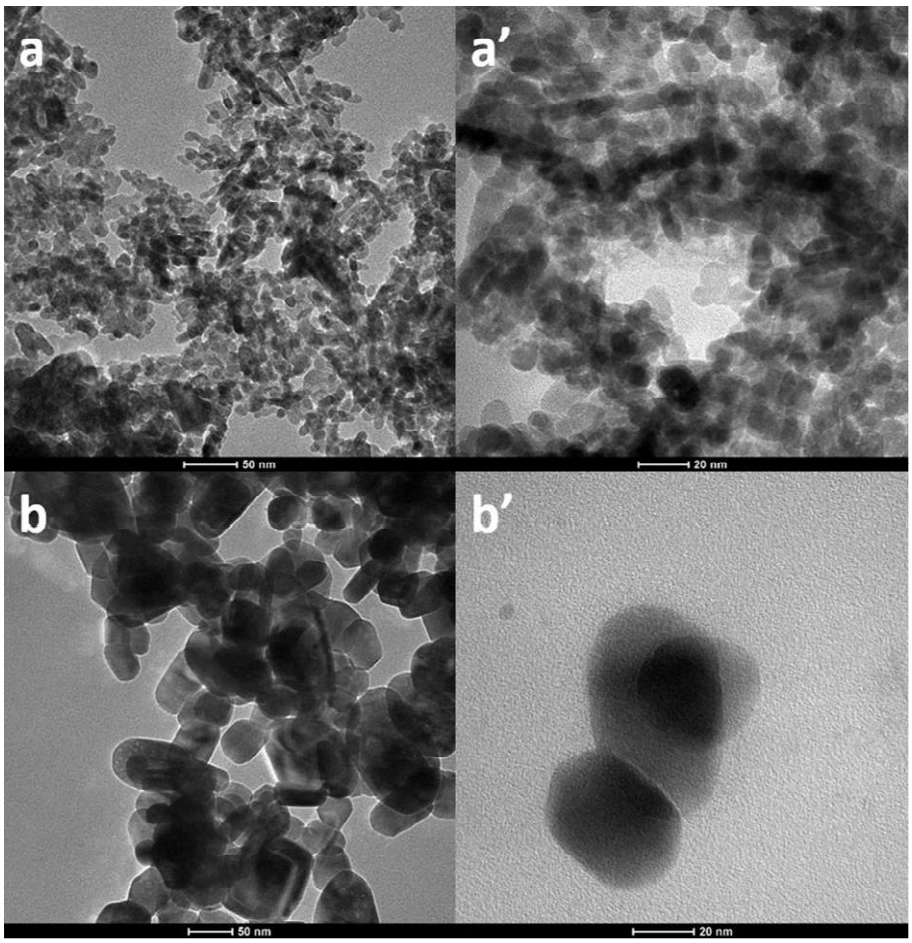


Figure 1. TEM images relevant to 300°C (a-a'), and 600°C (b-b')-calcined ZnO-NPs, electrochemically prepared in the presence of 1 g/L PSS in 30 mM $NaHCO_3$.

Transmission electron microscopy (TEM) characterization presented in Fig. 1 shows that the higher the calcination temperature, the larger is the nanoparticle diameter, as expected based on previous literature [18]. On the other hand, the good morphology of NPs confirms that the addition of PSS allows controlling NP size and shape. Moreover, the surface and bulk chemical compositions of calcined NPs were investigated by means of X-ray photoelectron (XPS) and Fourier transform infrared (FTIR) spectroscopies, respectively. Element abundances, expressed in terms of surface atomic% (surface At%), relevant to nanocatalysts calcined at 300°C and 600°C are reported in Fig. 2.

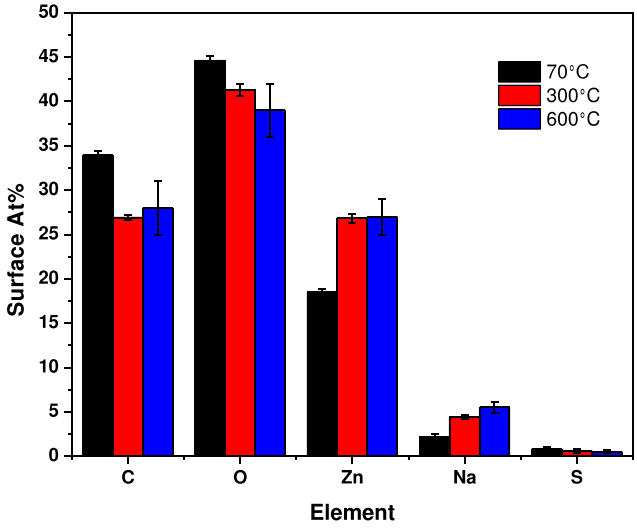


Figure 2. Surface chemical compositions (expressed as At%) of dried (black bars), 300°C-calcined (red bars), and 600°C-calcined (blue bars) nanomaterials, as determined by XPS analysis.

Values determined on samples dried at 70°C, not subjected to calcination, are also shown in the same figure, for comparison purposes. In all the cases, carbon, oxygen, zinc, sodium, and sulphur are identified and can be ascribed to the chemicals involved in the synthesis (e.g. sodium bicarbonate, zinc, PSS). Interestingly, sulphur is present at limit of quantification even at 600°C, suggesting a certain retention of the polymeric stabilizer. In fact, $S2p_{3/2}$ signal does not change position (Binding Energy, BE = 168.2 ± 0.2 eV) and line shape being undoubtedly associated to the sulphonate groups of PSS [19]. Moreover, the ratio between oxygen (as oxide) and zinc corroborates the hypothesis that stoichiometry of ZnO-NPs improves at higher calcination temperatures as this value changes from

0.81 ± 0.03 –for calcination at 300°C- to 1.02 ± 0.04, for powders treated at 600°C. By contrast, samples dried at 70°C did not show a component ascribable to zinc oxide, as O1s signal fell typically at BE compatible with zinc hydroxides and basic carbonates. In accordance to XPS results, FTIR investigation of calcined samples (Fig. 3) demonstrates that the stretching of Zn-O bond at about 460 cm^{-1} is more intense for 600 °C than for 300 °C-calcined nanocatalysts, indicating that conversion to ZnO-NPs is more effective in the latter case. Moreover, the band at about 3450 cm^{-1}, associated to hydroxyl groups and adsorbed water, is slightly visible only for 300 °C treated nanopowders. 300°C and 600 °C calcined ZnO-NPs were then employed as nanostructured catalysts, as illustrated in the following paragraphs.

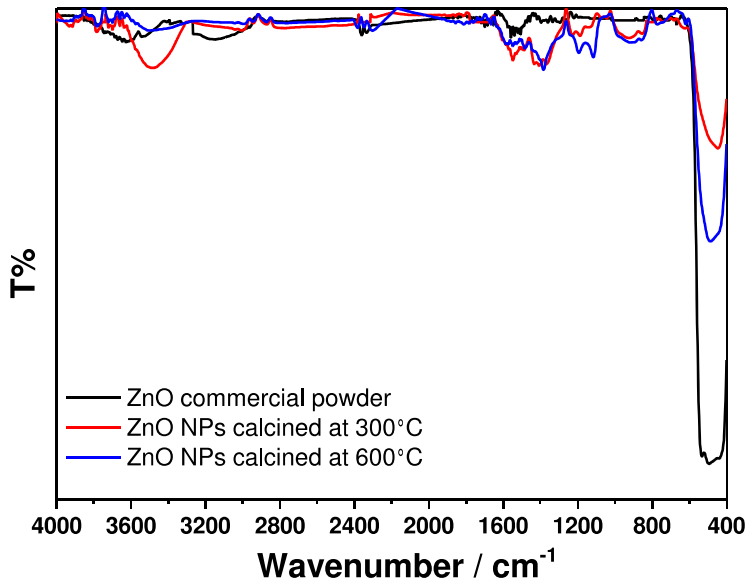


Figure 3. FTIR spectra relevant to ZnO-NPs treated at 300°C (red curve), or at 600°C (blue curve). Spectrum for commercial ZnO (black curve) is reported for comparison.

3.2. Preliminary catalytic tests

Catalysis conditions were surveyed on the model reaction between PC-BPA and 1,2-propandiol as a nucleophile (1,2-PD). This transesterification leads to the retro-polymerization process releasing BPA monomer and incorporating carbon monoxide into the glycol according to a high atom economy reaction (fig. 4). Beside the cyclic carbonate 4-methyl-1,3-dioxolan-2-one, a number of by-products could be formed (such as phenol, esters, etc.) coming from degradation of BPA dependently on the reaction conditions.

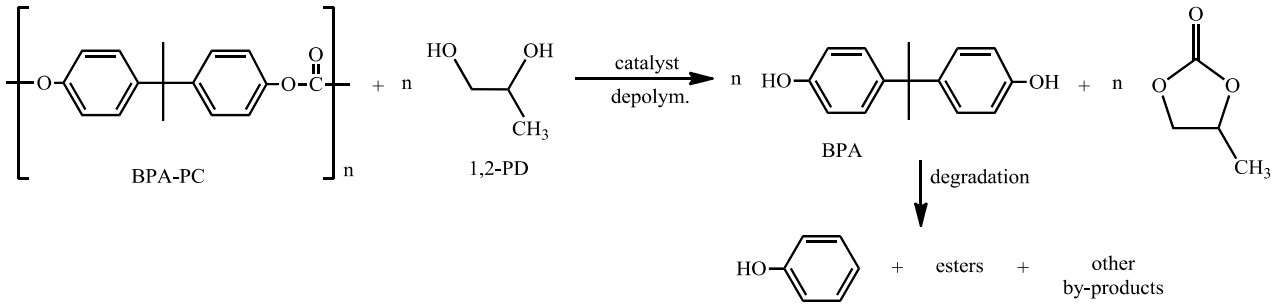


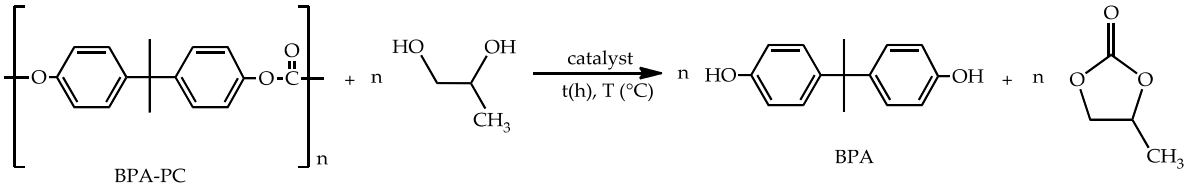
Figure 4. Depolymerization of bis-phenol A polycarbonate with 1,2-PD.

Reaction parameters were calibrated to process 2 mmol of polymer in 5 mL of THF with IL and/or other additives as catalytic system (generally 5 mol%). The screened range of temperatures was 80 ÷ 140 °C. Higher temperatures resulted in better conversions, but generally in lower selectivities. Reaction times were carefully regulated to limit BPA degradation (maximum 3 ÷ 7 hours dependently on the temperature conditions). The most representative results of this preliminary screening are summarized in table 1.

Initially, we paid attention to the sole basic catalysis by checking activity of common organic bases like pyridine, butylamine and proton sponges. In all cases, despite the high temperatures (140 °C), after 3 hours conversions did not exceeded 53%, while for longer reaction times by-products formation became the predominant process (table 1, runs 2-4).

Next, we decided to exploit the basic properties of ionic liquids investigating a variety of the most common tetraalkylammonium- and imidazolium salts. Among them, the former proved to be the most efficient ones (table 1, entries 5-11), probably due to the lower solvation effect exerted by the bulkier and shielded tetraalkylammonium cations towards their counter-anions, thus enhancing basicity of these latter. As expected, reactivity of ILs was profoundly affected by the nature of the anion. For instance, tetraalkylammonium ILs bearing AcO^- and Cl^- anions were found to promote depolymerization much better than the analogous ones with Br^- and I^- (table 1, entries 5-8). Correspondingly, [Bmim]AcO displayed better performance than [Bmim]Cl and [Bmim]Br (Table 1, runs 9-11).

Table 1. Preliminary catalytic tests[a]



Entry	Catalyst	T (°C)	time (h)	Conversion[b] (%)	Selectivity[c] (%)
1	-	140	3	0	-
2	Py	140	3	30%	100%
3	^{t}BuNH$_2$	140	3	50%	100%
4	"Proton sponge"[d]	140	3	53%	100%
5	NBu$_4$OAc	140	3	99%	80%
6	NBu$_4$Cl	140	3	98%	82%
7	NBu$_4$Br	140	3	95%	70%
8	NBu$_4$I	140	3	80%	99%
9	[Bmim]AcO	140	3	90%	80%
10	[Bmim]Cl	140	3	40%	99%
11	[Bmim]Br	140	3	30%	97%
12	NBu$_4$Cl	100	7 days	99%	100%
13	NBu$_4$Cl + CuO	100	7	35%	100%
14	NBu$_4$Cl + ZnO[e]	100	7	38%	100%
15	NBu$_4$Cl + CuCl$_2$	100	7	50%	100%
16	NBu$_4$Cl + ZnCl$_2$	100	7	70%	100%
17	**NBu$_4$Cl + ZnO-NPs[f]**	**100**	**7**	**98%**	**100%**
18	NBu$_4$Cl + ZnO-NPs[f]	100	3	60%	100%
19	NBu$_4$Cl + ZnO-NPs[g]	100	3	38%	100%
20	[Bmim]AcO + ZnO-NPs[f]	100	7	98%	99%
21	NBu$_4$Cl + ZnO-NPs[g]	100	7	93%	100%
22	NBu$_4$Cl + ZnO-NPs[f]	80	18	98%	100%
23	ZnO[e]	100	7 days	33%	100%
24	ZnO-NPs[f]	100	7 days	98%	99%

[a] Reaction conditions: BPA-PC (2 mmol), cat (5 mol%); IL (5 mol%), THF (5 mL/mmol PC). [b] Based on the glc areas ratio between BPA monomer and end capper molecule 2-phenoxy-cumene (see experimental section); [c] Based on glc areas of all by-products; [d] 1,8-Bis(dimethylamino)naphthalene. [e] ZnO commercial bulk powder; [f] ZnO nanoparticles calcined at 600°C; [g] ZnO nanoparticles calcined at 300 °C.

Recently, a similar effect was observed by us for the N-alkylation of arylamines in ionic liquids [20] and interpreted as reflecting the capability of the IL anions to accept a hydrogen bond.

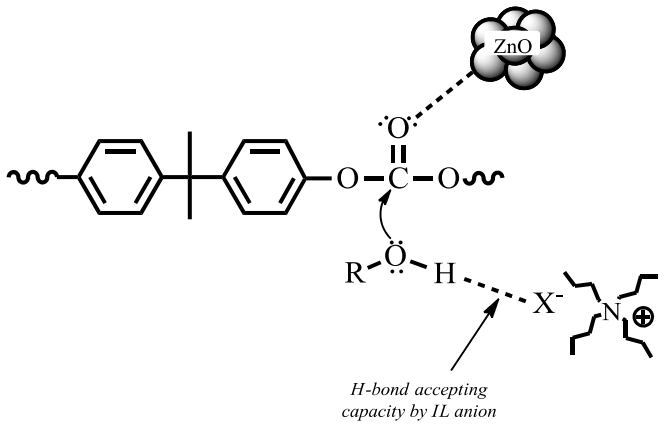
Similarly, these early results on PC depolymerization seem to be in good agreement with a mechanism connected with the ability of the IL anions to accept a hydrogen bond form propylene glycol, thus enhancing its nucleophilicity. Such a hydrogen-bond basicity can be quantitatively expressed by Kamlet–Taft β parameters for ILs: 1.16 (AcO^-), 1.00 (Cl^-), 0.67 (Br^-), 0.37 (BF_4^-), 0.30 (I^-), 0.21 (PF_6^-) [21] (fig. 5).

In line with this assumption, better performances emerged in the case of tetraalkylammonium salts bearing acetate or chloride ions as basic catalyst (NBu_4OAc or NBu_4Cl). In these cases, retro-polymerization occurred in only 3 hours without metals or any other co-catalysts (table 1, entries 5 and 6). Unfortunately, selectivities towards BPA proved to be incomplete (~ 80%) and conversions dropped at temperatures below 140 °C (Table 1, run 12).

To overcome this drawback, we turned out attention to Lewis acids in order to enhance electrophilicity of the polymer carbonyl group and exploit their synergic combination with a good H-bonding acceptor anion of a tetraalkylammonium salt (fig. 5).

X	β
AcO-	1.16
Cl-	1.00
Br-	0.67
BF_4-	0.37
I-	0.30
PF_6-	0.21

IL anions Kamlet–Taft parameters



IL	Yield
NBu_4OAc	99%
NBu_4Cl	98%
NBu_4Br	95%
NBu_4I	80%
[Bmim]OAc	90%
[Bmim]Cl	40%
[Bmim]Br	30%

PC depolymerization

Figure 5. Synergic combination of a bifunctional acid/basic catalyst composed by nanostructured ZnO and NBu_4Cl. Performance of IL as basic co-catalyst is related to the H-bond accepting ability of its anions (mainly AcO^- and Cl^-) expressed by the Kamlet-Taft parameters.

With this in mind, we explored bifunctional basic/acid catalysts composed by NBu_4Cl and Cu or Zn chlorides (or their bulk oxide powders) obtaining the depolymerization process with a complete selectivity towards the expected products at 100 °C. Notably, chlorides proved to be more efficient than oxides and $ZnCl_2$ was more reactive than $CuCl_2$ (table 1, runs 13-16).

However, albeit the milder conditions and improved selectivity, conversions proved to be still unsatisfactory (35% ÷ 70 %). In addition, all attempts to recover and re-use the catalyst system $ZnCl_2/NBu_4Cl$ failed, probably due to the good solubility of these salts in THF.

These problems were all circumvented replacing bulk zinc materials with nanostructured catalysts by virtue of their high surface area. Indeed, while commercial bulk ZnO powder still provided disappointing results (Table 1, entry 14), the new assembled bifunctional catalyst ZnO-NPs/NBu_4Cl enabled not only the complete PC depolymerization to propylene glycol carbonate and BPA in 7 hours at 100 °C, but also a whole catalyst recovery and its prompt re-use (see Table 1, entry 17 and section 2.6).

Of particular concern was the influence of calcination temperature employed to prepare ZnO colloids. Indeed, the best catalytic performances were displayed by the bigger ZnO nanoparticles calcined at 600 °C (fig. 1), in contrast to the smaller and less active ZnO nanoparticles treated at 300 °C (Table 1, entries 17-21). This different activity was probably due to the lower sulphur residue percentages of PSS surfactant present on colloids treated at 600 °C, as emerged by element abundances obtained by surface chemical composition analyses (fig. 2).

Similar results were obtained both with the assembled bifunctional catalyst composed by [Bmim]OAc as the base and calcinated ZnO nanoparticles as Lewis acid counterpart (Table 1, entries 20-21). On the contrary, reactions carried out at lower temperatures (80 °C), as well in the absence of the IL co-catalyst (NBu_4Cl), required longer reaction times, thus emphasizing the synergistic effect exerted by both metal oxide and IL (Table 1, entries 22-24).

3.3. Effect of nucleophile/PC ratio

As expected, excess amounts of nucleophiles were found to be necessary to reach a high depolymerization efficiency. The influence of nucleophile/PC molar ratio is elucidated in figure 6 in the case of BPA-PC hydrolysis (water as the nucleophile). Excess amounts of water were calculated based on the average number of the polymer carbonyl functionalities. As can be seen, depolymerization reached the maximum conversion with an excess amount of 30 equivalents of H_2O.

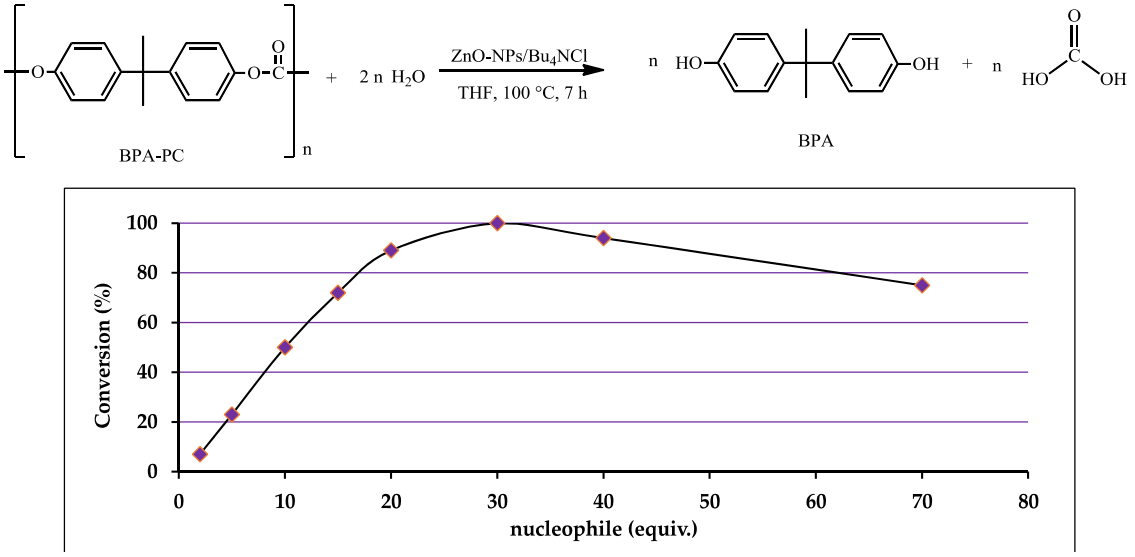


Figure 6. Reaction of BPA-PC with water promoted by ZnO (nano): influence of Nu / PC ratio. Reaction conditions: THF, 100°C, 7h, Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%).

A similar trend was also observed in the case of methanolysis. In the presence of reactants bearing twice nucleophilic sites such as diols (or glycerol) and diamines, the best Nu/PC ratio was approximately 14. In all cases, too large excess amounts of nucleophiles proved to be detrimental for reaction, probably due to the increase of the polarity of the medium and the consequential decreases of solubility of the low polar polymer.

3.4. Alcoholysis and aminolysis of BPA-PC

With the optimized conditions in hand, we performed a series of alcoholysis and aminolysis experiments of BPA-PC in which the polymer was used as a carbonylating agent alternative to phosgene, thus producing relevant fine chemicals like carbonates and ureas in high yields (table 2).

These products are useful compounds that find application in many practical fields. Carbonates are successfully employed as solvents [22] and as intermediates in the synthesis of agrochemicals, pesticides, and pharmaceuticals [23]. Ureas are used as dyes for cellulose fibers, antioxidants in gasoline, corrosion inhibitors, plant growth regulators, pesticides, insecticides, and as tranquilizing and anticonvulsant agents [24].

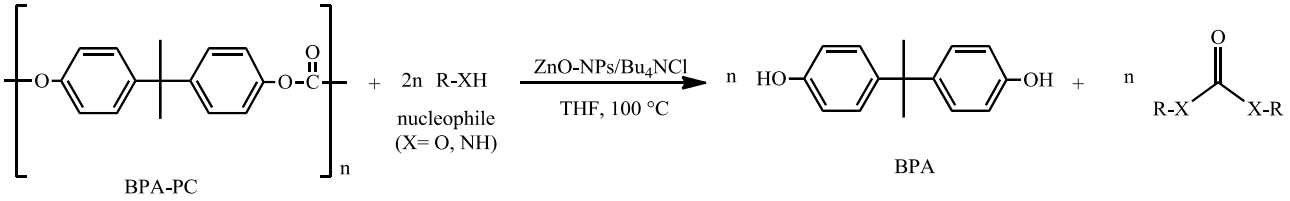
ZnO nanocatalyst in combination with NBu_4Cl displayed good activity under moderate conditions. With methanol as the nucleophile, isolation of dimethylcarbonate (DMC) product required more complex procedures, due to the formation of a THF/CH_3OH azeotropic mixture (Table 2, entry 1).

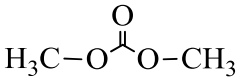
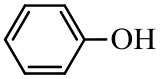
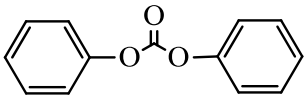
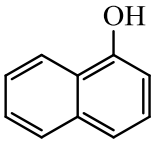
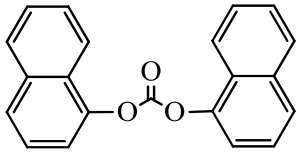
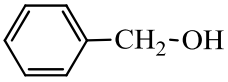
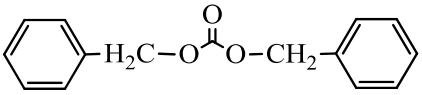
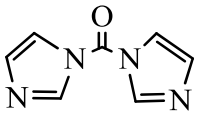
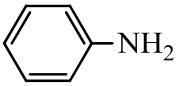
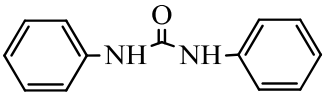
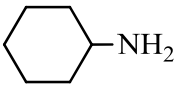
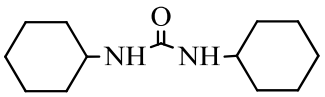
A remarkable result was obtained in the case of phenol as the nucleophile (table 2, entry 2). In the literature, BPA-PC transesterification reactions with phenols to form diarylcarbonates have been extensively studied [25]. However, most of the proposed methods necessitate of a relatively large amounts of basic catalysts such as hydroxides, and the depolymerization rate was relatively low resulting in poor yields and limited catalyst recycle.

Diphenylcarbonate (DPC), a valuable starting material useful to produce polycarbonate by molten transesterification with BPA [26], is typically obtained from DMC by transesterification with phenol. However, high yields of DPC are rarely obtained being this reaction severely equilibrium limited. DPC can be also obtained from phenol and CO_2 using molecular or heterogeneous catalysts [27].

With method proposed here, good yields of DPC, as well as of dinaphthylcarbonate, can be obtained from the waste polycarbonate by using a very simplified procedure and relatively mild conditions (Table 2, entries 2-3).

Table 2.
ZnO-NPS/NBu_4Cl catalysed alcoholysis/aminolysis of PC:
synthesis of linear carbonates and ureas[a]



Entry	Nucleophile (R-OH or R-NH_2)	Linear carbonates or ureas products	Yields (%)[b]
1	CH_3OH		> 99 (97)[c]
2			> 99% (98%)[d]
3			> 99%
4			> 99%
5			> 99%
6			> 99% (96%)[d]
7			> 99% (97%)[d]

[a] Reaction conditions: THF 5 mL/mmol of PC; Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%), PC 2 mmol, 7 hrs, 100°C. [b] GLC yield based on calibration curves (for details see experimental section). [c] In brackets, isolated yield as azeotrope. [d] In brackets, isolated yields.

Another interesting product such as dibenzylcarbonate (DBnC) can be easily obtained with our strategy in an economical way (Table 2, entry 4). DBnC, which is used in pharmaceutical and fine chemical industry as protecting group instead of toxic benzyl halides, is a highly costly product (with prices ranging from 30 to 350 times more higher than other alkyl or aryl carbonates) [28].

Tundo et al [29] proposed a straightforward catalytic protocol for the synthesis of DBnC via transesterification of the precious DMC. With our method, DBnC can be directly obtained from a plastic waste with clear economic advantages.

When N-nucleophiles were used in place of alcohols, PC was smoothly depolymerized furnishing the corresponding ureas. These compounds can be accessed by reaction of phosgene with primary or secondary amines, by direct metal-catalyzed oxidative carbonylation of amines [30] and other protocols [31].

Under the presented conditions, PC was depolymerized giving linear aryl and alkyl ureas in excellent yields together with BPA as by-product (Table 2, entries 5-7). Reaction proceeded smoothly even with weaker nucleophiles such as aromatic amines. For instance, in case of aniline, diphenylurea – a key intermediate in the preparation of 4,4'-diisocyanatephenylmethane (MDI) [32] – was obtained in 96% of yield (after re-crystallization) without increasing temperature or prolonging reaction time (Table 2, entry 6).

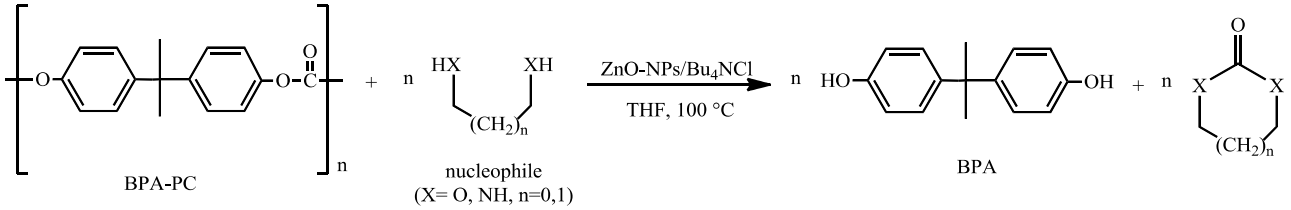
3.5. Synthesis of cyclic derivatives

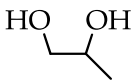
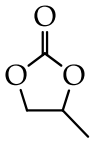
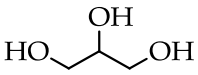
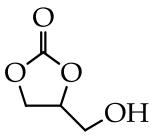
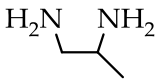
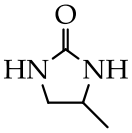
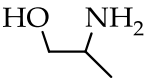
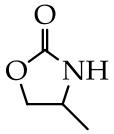
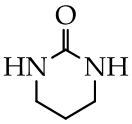
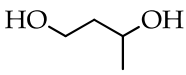
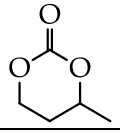
When diols, aminols and diamines were used as nucleophiles, precious cyclic carbonyl derivatives such as 2-dioxolanones, 2-oxazolidinones and cyclic ureas were obtained, respectively (table 3). These latter are key subunits of bioactive molecules [33] and many six membered rings ureas possess anticancer [34] or antiviral [35] activities. Typically, cyclic ureas are synthesized by reaction of diamines with phosgene (or related products) [36], CO, CO_2 and CS_2 in the presence of metal catalysts [29, 37].

From the environmental point of view, reaction of scrap polycarbonate with diamines provides an attractive alternative method. Consequently, by following our proposed procedure, we reacted propane-1,2-diamine with PC to get five-membered cyclic ureas (Table 3, entry 3). Similarly,

propane-1,3-diamine furnished the corresponding tetrahydropyrimidinone in an almost complete conversion (Table 3, entry 5).

Table 3. Synthesis of cyclic carbonates and ureas[a)]



Entry	Nucleophile	Time (h)	Product	Yields (%)[b)]
1		7		98%
2		14		> 99 (97)
3		7		> 99 (98)
4		7		> 99 (97)
5		7		97 (96)
6		7		> 99

[a)] Reaction conditions: THF 5 mL/mmol of PC; Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%), PC 2 mmol, 7 hrs, 100°C. [b)] GLC yield based on calibration curves (for details see experimental section). In brackets, isolated yields.

By replacing diamines with diols or aminols, other high-value carbonyl derivative such as cyclic carbonates, 2-oxazolidinones and 1,3-dioxan-2-ones were achieved. Particularly attractive is the transformation of glycerol (the well-known waste product of biodiesel industry) into the

corresponding cyclic carbonate, a raw material that has gained much industrial interest as solvent, additive and chemical intermediate [38] (table 3, entry 2). A plethora of methods are available in the literature for the preparation of glycerol carbonate [39], but none of them, to the best of our knowledge, uses scrap polycarbonate as starting material. This process has a special symbolic value from the green chemistry point of view as it permits the simultaneous valorization of two industrial wastes, such as polycarbonates and glycerol, transforming them into valuable raw chemicals.

Under the same conditions, propylene glycol, 2-amino-1-propanol and butane-1,3-diol and were reacted in only 7 hours to give the corresponding cyclic carbonates and 2-oxazolidinone (table 3, entries 1,4,6). To widen the scope of the present work, a scale-up reaction was also performed. To this end, 15 grams of PC obtained from a wasted compact disc, were reacted in 7 hours with 1,3-diamine propane. With our delight, after 7 hours, 5.44 grams of the corresponding pure cyclic urea were isolated.

3.6. Catalyst recycling

Catalyst robustness was evaluated using polycarbonate hydrolysis as the model reaction. Being insoluble in THF, zinc oxide nanoparticles remained as precipitate at the end of the depolymerization and could be removed from the reaction medium by centrifugation, dried with a nitrogen stream and then reused by addition of the co-catalyst Bu_4NCl and fresh reagents (see experimental section).

In this way, the Lewis acid catalyst ZnO-NPs could be recycled up to five cycles with negligible loss of activity (fig. 7), whereas its basic counterpart Bu_4NCl was only partially recovered during the separation procedure and must be integrated with fresh co-catalyst after each run (see section 2.4).

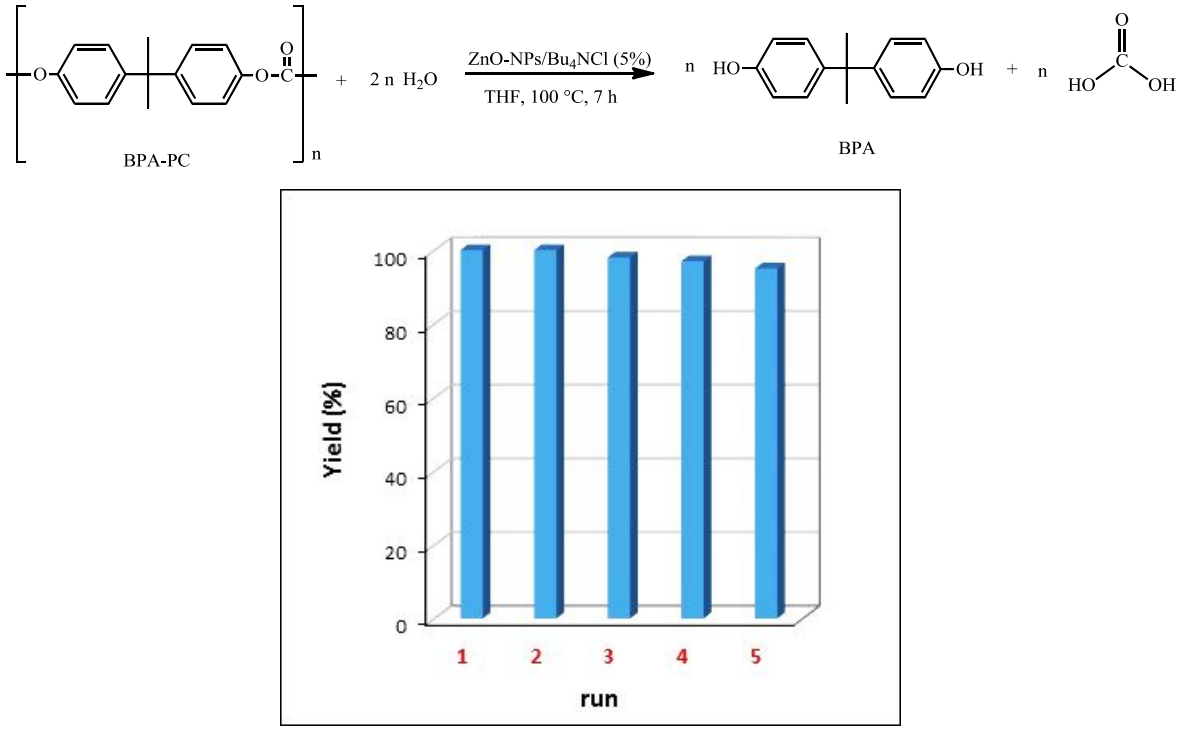


Figure 7. BPA-PC hydrolysis promoted by ZnO-NPs/Bu_4NCl: catalyst recycling.
Reaction conditions: THF, 100°C, 7h, Water (30 equiv.) Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%).

4. Conclusions

Chemical depolymerization has to be considered the most promising technique for recycling waste polymers and plastics, the sole allowing the conversion of plastics into their monomers or other valuable products. Alcoholysis and aminolysis are conventional procedures for chemical recycling of polycarbonates. With them it is possible not only the recovery of the starting monomer (BPA), but also the use of the polymer as carbonylating agent for the synthesis of valuable compounds, without wasting carbon dioxide.

Typically these processes are performed under hard conditions that require hot compressed water, alkaline solutions, supercritical ethanol, microwave irradiation, or metal catalysts such as $Mn(OAc)_2$, MgO and CaO.

The protocol presented here, unprecedented in the literature, is based on the double catalytic effect obtained by combining a nanostructured metal Lewis acid catalyst (ZnO-NPs) that would

enhance electrophilicity of carbonyl moiety, with a tetraalkylammonium ionic liquids (NBu_4Cl), in which the H-bond accepting ability of anion would enhance nucleophilicity of alcohols and amines, so favoring depolymerization at milder temperature conditions.

A complete depolymerization of polycarbonate occurs in seven hours at 100 °C and ZnO nanocatalysts can be recycled several times without sensible lack of activity.

Remarkably, when polycarbonate is reacted with glycerol it is completely converted into BPA and propylene glycol. This means that in a single process is possible to convert two industrial wastes (polycarbonate and glycerol) into two valuable chemicals like BPA (the monomer ready to be reused) and glycerol carbonate (a useful industrial solvent and fuel additive) [40].

Due to the simple and mild experimental procedure and the low cost of the easily recyclable co-catalysts, this protocol can compete with others of industrial importance.

Acknowledgment

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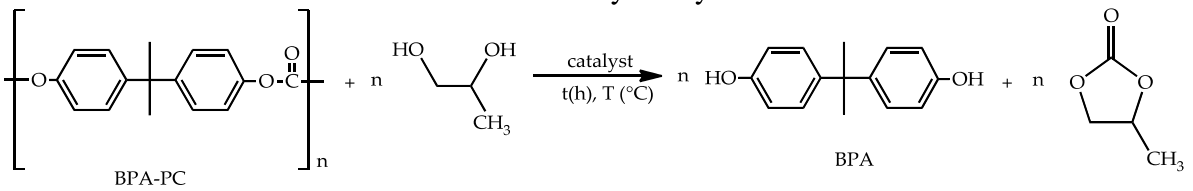
Table

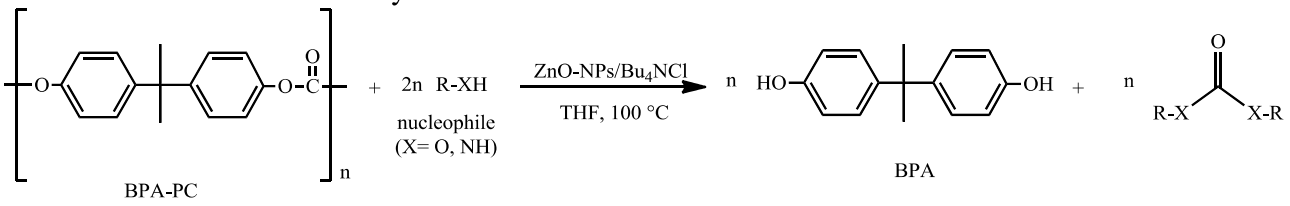
Table 1. Preliminary catalytic tests[a]

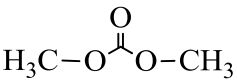
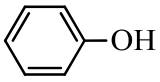
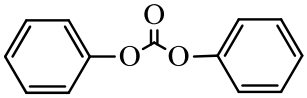
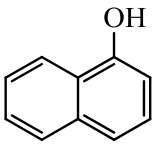
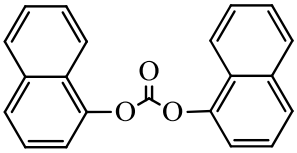
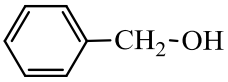
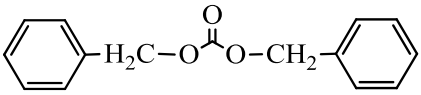
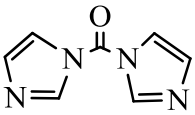
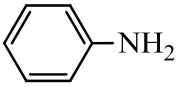
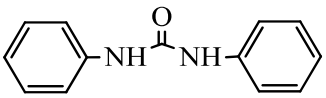
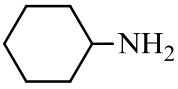
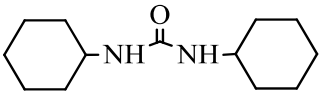


Entry	Catalyst	T (°C)	time (h)	Conversion[b] (%)	Selectivity[c] (%)
1	-	140	3	0	-
2	Py	140	3	30%	100%
3	^{t}BuNH$_2$	140	3	50%	100%
4	"Proton sponge"[d]	140	3	53%	100%
5	NBu$_4$OAc	140	3	99%	80%
6	NBu$_4$Cl	140	3	98%	82%
7	NBu$_4$Br	140	3	95%	70%
8	NBu$_4$I	140	3	80%	99%
9	[Bmim]AcO	140	3	90%	80%
10	[Bmim]Cl	140	3	40%	99%
11	[Bmim]Br	140	3	30%	97%
12	NBu$_4$Cl	100	7 days	99%	100%
13	NBu$_4$Cl + CuO	100	7	35%	100%
14	NBu$_4$Cl + ZnO[e]	100	7	38%	100%
15	NBu$_4$Cl + CuCl$_2$	100	7	50%	100%
16	NBu$_4$Cl + ZnCl$_2$	100	7	70%	100%
17	**NBu$_4$Cl + ZnO-NPs[f]**	**100**	**7**	**98%**	**100%**
18	NBu$_4$Cl + ZnO-NPs[f]	100	3	60%	100%
19	NBu$_4$Cl + ZnO-NPs[g]	100	3	38%	100%
20	[Bmim]AcO + ZnO-NPs[f]	100	7	98%	99%
21	NBu$_4$Cl + ZnO-NPs[g]	100	7	93%	100%
22	NBu$_4$Cl + ZnO-NPs[f]	80	18	98%	100%
23	ZnO[e]	100	7 days	33%	100%
24	ZnO-NPs[f]	100	7 days	98%	99%

[a] Reaction conditions: BPA-PC (2 mmol), cat (5 mol%); IL (5 mol%), THF (5 mL/mmol PC). [b] Based on the glc areas ratio between BPA monomer and end capper molecule 2-phenoxy-cumene (see experimental section); [c] Based on glc areas of all by-products; [d] 1,8-Bis(dimethylamino)naphthalene. [e] ZnO commercial bulk powder; [f] ZnO nanoparticles calcined at 600°C; [g] ZnO nanoparticles calcined at 300 °C.

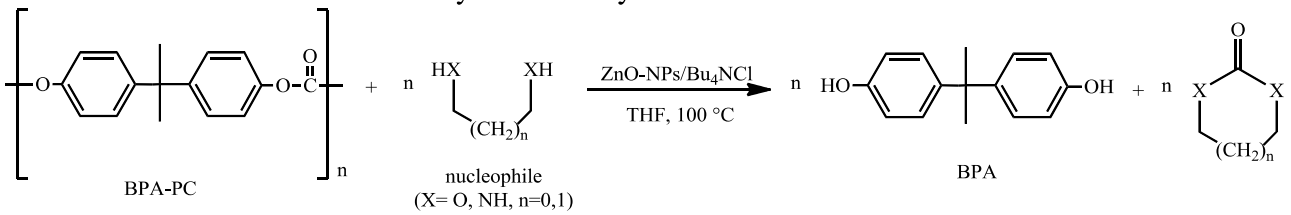
Table 2.
ZnO-NPS/NBu_4Cl catalysed alcoholysis/aminolysis of PC:
synthesis of linear carbonates and ureas[a]

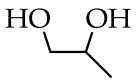
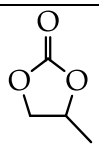
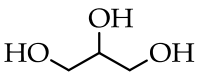
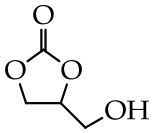
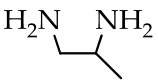
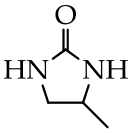
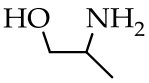
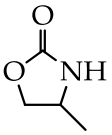
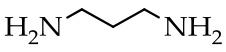
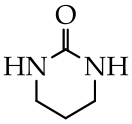
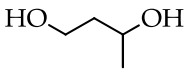
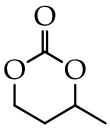


Entry	Nucleophile (R-OH or R-NH_2)	Linear carbonates or ureas products	Yields (%)[b]
1	CH_3OH		> 99 (97)[c]
2			> 99% (98%)[d]
3			> 99%
4			> 99%
5			> 99%
6			> 99% (96%)[d]
7			> 99% (97%)[d]

[a] Reaction conditions: THF 5 mL/mmol of PC; Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%), PC 2 mmol, 7 hrs, 100°C. [b] GLC yield based on calibration curves (for details see experimental section). [c] In brackets, isolated yield as azeotrope. [d] In brackets, isolated yields.

Table 3. Synthesis of cyclic carbonates and ureas[a)]



Entry	Nucleophile	Time (h)	Product	Yields (%)[b)]
1		7		98%
2		14		> 99 (97)
3		7		> 99 (98)
4		7		> 99 (97)
5		7		97 (96)
6		7		> 99

[a)] Reaction conditions: THF 5 mL/mmol of PC; Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%), PC 2 mmol, 7 hrs, 100°C. [b)] GLC yield based on calibration curves (for details see experimental section). In brackets, isolated yields.

Figure

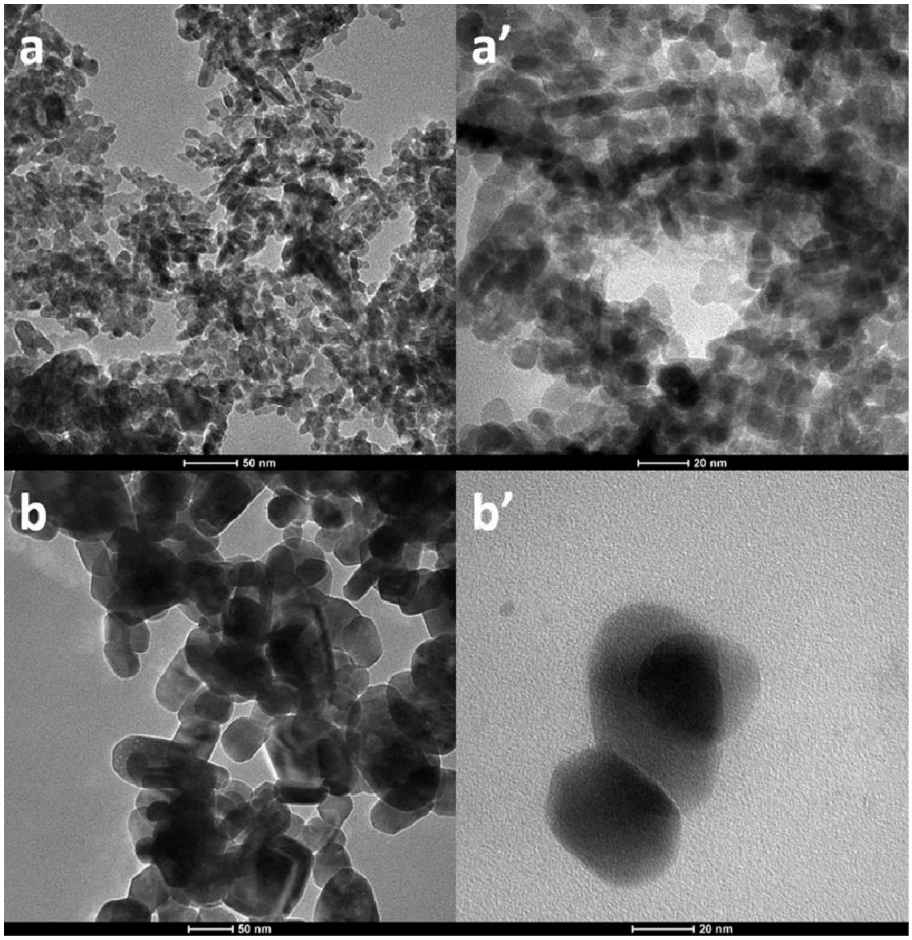


Figure 1. TEM images relevant to 300°C (a-a'), and 600°C (b-b')-calcined ZnO-NPs, electrochemically prepared in the presence of 1 g/L PSS in 30 mM $NaHCO_3$.

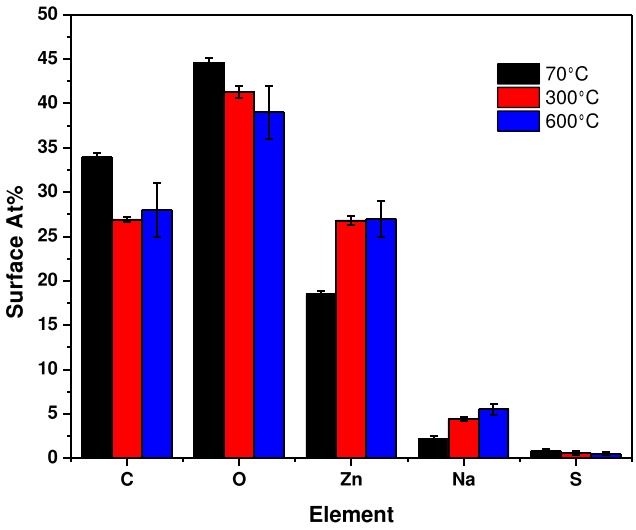


Figure 2. Surface chemical compositions (expressed as At%) of dried (black bars), 300°C-calcined (red bars), and 600°C-calcined (blue bars) nanomaterials, as determined by XPS analysis.

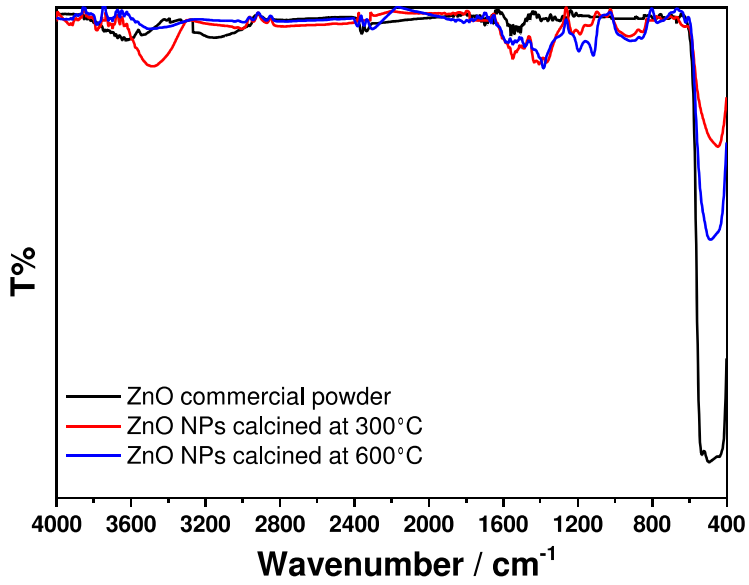


Figure 3. FTIR spectra relevant to ZnO-NPs treated at 300°C (red curve), or at 600°C (blue curve). Spectrum for commercial ZnO (black curve) is reported for comparison.

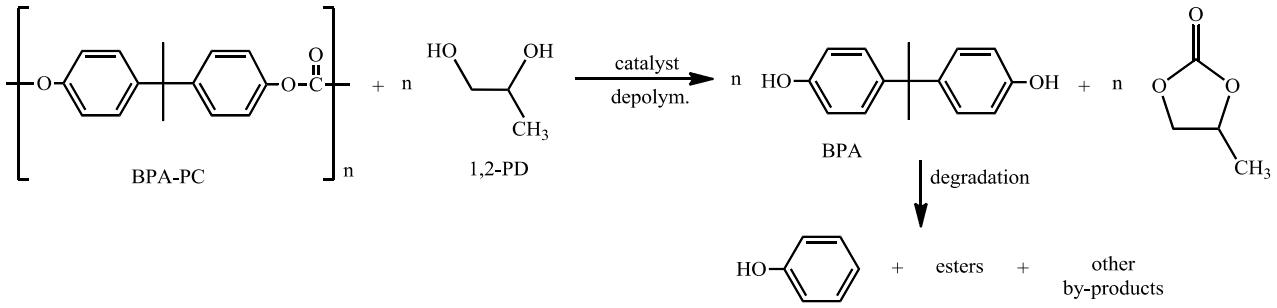
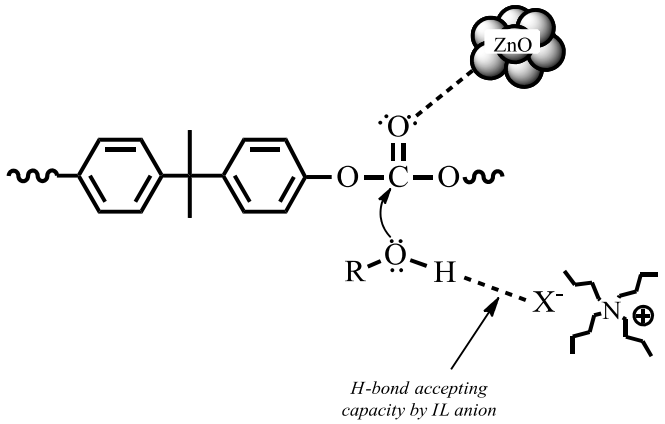


Figure 4. Depolymerization of bis-phenol A polycarbonate with 1,2-PD.

X	β
AcO-	1.16
Cl-	1.00
Br-	0.67
BF_4-	0.37
I-	0.30
PF_6-	0.21

IL anions Kamlet–Taft parameters



IL	Yield
NBu_4OAc	99%
NBu_4Cl	98%
NBu_4Br	95%
NBu_4I	80%
[Bmim]OAc	90%
[Bmim]Cl	40%
[Bmim]Br	30%

PC depolymerization

Figure 5. Synergic combination of a bifunctional acid/basic catalyst composed by nanostructured ZnO and NBu_4Cl. Performance of IL as basic co-catalyst is related to the H-bond accepting ability of its anions (mainly AcO^- and Cl^-) expressed by the Kamlet-Taft parameters.

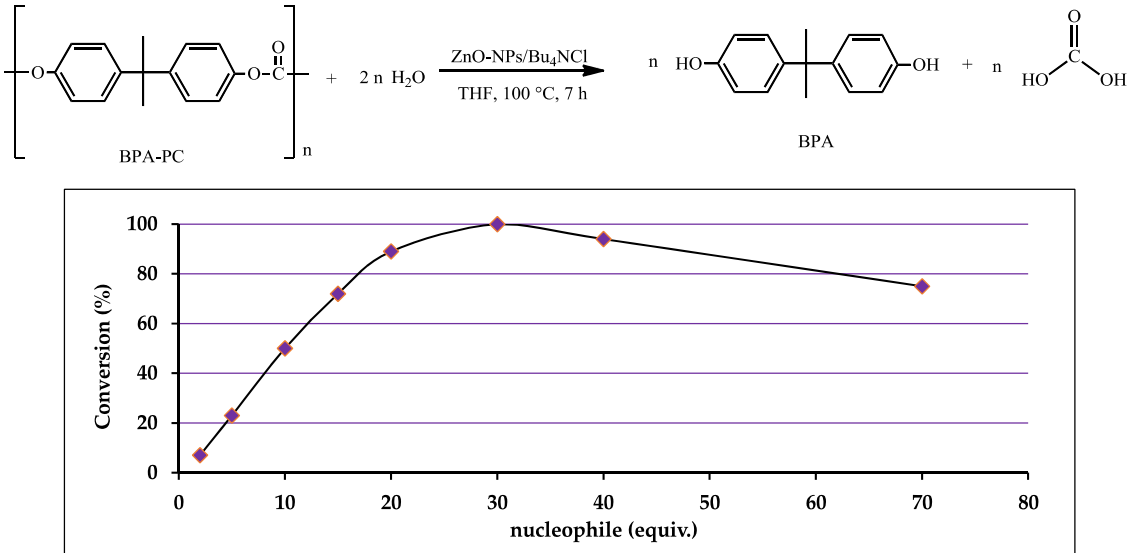


Figure 6. Reaction of BPA-PC with water promoted by ZnO (nano): influence of Nu / PC ratio. Reaction conditions: THF, 100°C, 7h, Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%).

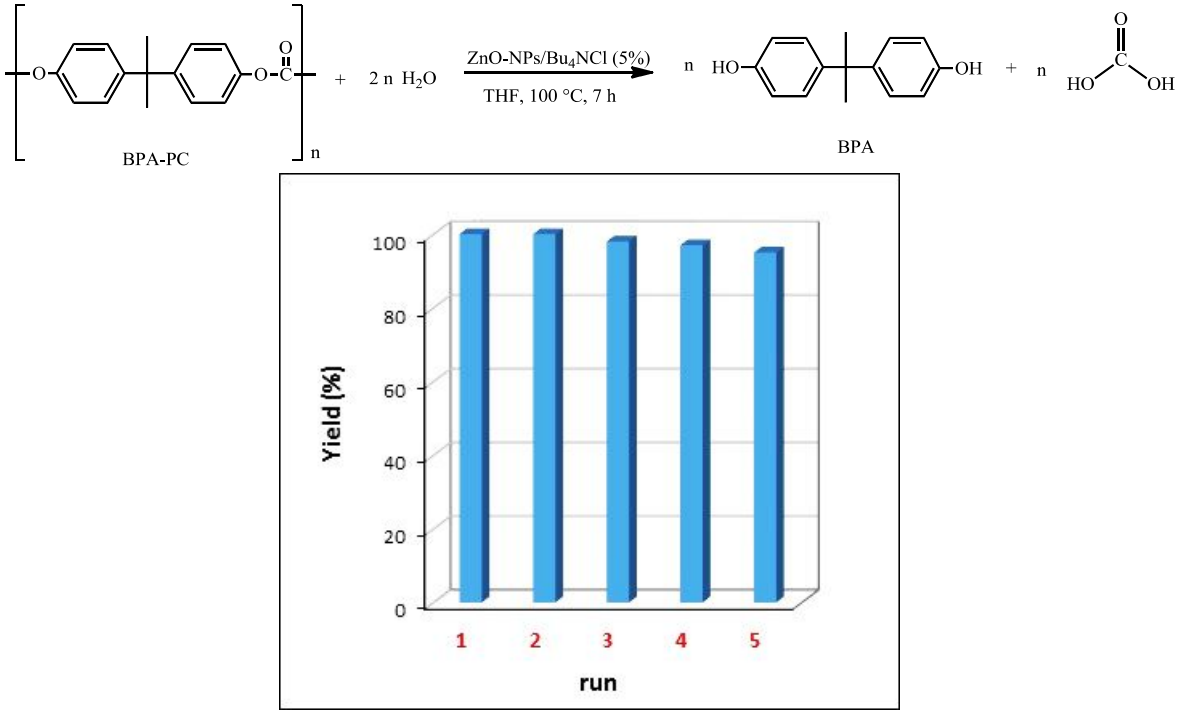


Figure 7. BPA-PC hydrolysis promoted by ZnO-NPs/Bu_4NCl: catalyst recycling.
Reaction conditions: THF, 100°C, 7h, Water (30 equiv.) Zn / BPA-PC ≈ 5 mol%, NBu_4Cl (5 mol%).

Supplementary material

Ionic liquids/ZnO Nanoparticles as Recyclable Catalyst for Polycarbonate Depolymerization

Francesco Iannone[a], Michele Casiello[a,*], Antonio Monopoli[a] , Pietro Cotugno[a,*], Maria Chiara Sportelli[a], Rosaria Anna Picca[a], Nicola Cioffi[a], Maria M. Dell'Anna[c], and Angelo Nacci[a,b,*]

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Contents:

S1. Evaluation of depolymerization percentage 2

S2. Isolation and identification of carbonylated reaction products.....3

S1. Evaluation of depolymerization percentage

Depolymerization percentages reported in Tables 1-3 were determined measuring the ratios of the chromatographic areas between the BPA starting monomer and the 4-(2-phenylpropan-2-yl)phenol, that is the end capping agent for the Sigma-Aldrich BPA-PC.

Generally, in the polymers production the end-capping agent is added when a desired medium molecular weight is achieved, to stop the polymerization reaction [1]. In the case of Sigma-Aldrich BPA-PC, the molar ratio of the end-capping agent respect to polymer is about the 3%, as preliminary determinated by ^{1}H-NMR analysis.

Based on the assumption that the end-capping agent is immediately released into the reaction medium during the depolymerization process, it can be considered its concentration to be constant. In this way, it is possible to use the end-capping agent (ECA) as an internal standard.

Considering true this equation:

$$A_{BPA}/A_{ECA} = N_{BPA}/N_{ECA}$$

where A_{BPA} and A_{ECA} are the chromatographic areas of the bis phenol A and the end capping agent, respectively, while N_{BPA} and N_{ECA} are the corresponding molar amounts, we can calculate approximately the molar amount of bisphenol A formed by the reverse formula:

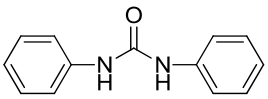
$$N_{BPA} = N_{ECA} (A_{BPA}/A_{ECA})$$

and then calculate the conversion percentage.

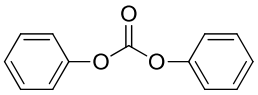
S2. Isolation and identification of carbonylated reaction products

Carbonylated compounds (carbonates, ureas and urethanes) listed in tables 1-3 were identified by comparison of their spectral data (MS and NMR reported below) with those reported in the literature. For isolated products (in brackets in yields columns) the separation procedure is also described.

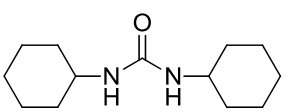
1,3-diphenylurea. After reaction, the aqueous solution was mixed with aqueous $NaHCO_3$ under vigorous stirring. The organic layer was then extracted with chloroform, dried over anhydrous Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from chloroform and hexane gave 1,3-diphenylurea as a white solid in 96% of yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 2H), 6.92-6.96 (t, 2H), 7.21-7.25(t, 4H), 7.48-7.50 (d, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 91.43, 94.93, 101.55, 178.2. MS m/z (%): 210 (M^+, 14), 120 (15), 91 (100). Lit. [2].



Diphenylcarbonate. The reaction mixture was mixed with aqueous $NaHCO_3$ under vigorous stirring. Then, after extraction with chloroform, the organic phase was dried over anhydrous Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from chloroform and hexane gave diphenylcarbonate as a white solid in 98% of yield. ^{1}H NMR (400 MHz, $CDCl_3$) 7.28-7.31 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (400 MHz,$CDCl_3$) δ 121.2, 126.58, 129.86, 151.28. MS m/z (%) 214 (M^+, 75), 170 (50), 141 (55) 79 (100). Lit. [3].

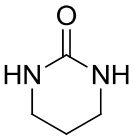


Dicyclohexyl urea. After the end of reaction, mixture contained dicyclohexyl urea precipitated that was filtered furnishing a white solid in 96% of yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98-1.13 (m, 6H), 1.19-1.30 (m, 4H), 1.46-1.51(m, 2H), 1.58–1.63 (m, 4H), 1.72-1.76 (m,4H), 3.20 (q,2H), 3.31-3.38 (s,2H); ^{13}C NMR (400

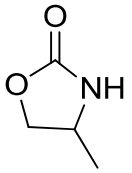


MHz,$CDCl_3$) δ 7.66, 8.35, 12.29, 16.36,189.85. GLC-MS 224 (M^+, 21), 143 (20), 99 (35), 56 (100). Lit. [4].

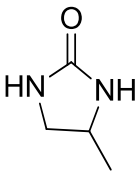
Tetrahydropyrimidin-2(1H)-one. After the end of reaction, mixture contained Tetrahydropyrimidin-2(1H)-one precipitated that was filtered furnishing a white solid in 96% of yield.. ^{1}H NMR (400 MHz, CD_3OD) δ 2.75-2.85 (sext, 2H), 4.20-4.30 (q, 4H); ^{13}C NMR (400 MHz, CD_3OD) δ 22.19, 40.75, 208.16. MS m/z (%) 100 (M^+, 76), 56 (10), 30 (100). Lit. [5].



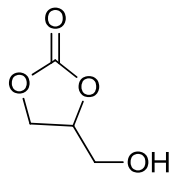
4-methyloxazolidin-2-one. Reaction mixture was extracted with chloroform. Evaporation of solvent, followed by purification by short column-chromatography (AcOEt/MeOH 1:1) gave the product as an oil. IR (neat) 3300, 1745, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J= 6 Hz, 3H), 2.50 (t, J= 8 Hz, 1H), 2.84 (t, J= 8 Hz, 1H), 3.66–3.71 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.75, 49.16, 68.41, 154.81. MS m/z (%) 101 (M^+, 100), 86 (26), 73 (13), 56 (27). Lit. [4a].



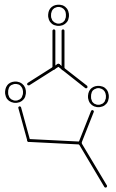
4-Methyl-2-imidazolidone. Reaction mixture was extracted with chloroform. Evaporation of solvent, followed by purification by short column-chromatography (AcOEt/MeOH 1:1) gave the product as a solid. Mp 118 °C. IR (KBr) 3215, 1695, 1260 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.2 (d, J= 6 Hz, 3H), 2.72–2.88 (m, 1H), 3.03-3.07 (m, 1H), 3.55–3.60 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.16, 31.03, 41.53, 153.76. MS m/z (%) 100 (M^+, 84), 85 (100). Lit. [6].



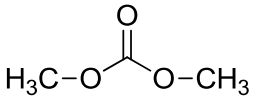
Glycerol carbonate. Reaction mixture was extracted with chloroform. Evaporation of solvent, followed by purification by short column-chromatography (MeOH) gave the product. ^{1}H NMR (400 MHz, D_2O) δ 3.61-3.68 (dd, 1H), 3.80-3.86 (dd, 1H), 4.31-4.37 (qq, 1H), 4.54–4.60 (tt, 1H), 4.86-4.94 (m,1H). ^{13}C NMR (400 MHz, D_2O) δ 60.91, 66.82, 70.038, 157.69. MS m/z (%) of silylated glycerol carbonate: 189 (M^+−1, >5), 160 (>5), 145 (>5), 131 (48), 116 (4), 103 (26),101 (100), 73 (76). Lit. [7].



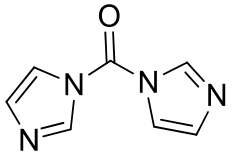
4-methyl-1,3-dioxolan-2-one. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR. The spectrum showed the presence of a strong absorptions around 1800 cm^{-1} assigned to cyclic carbonates 4-methyl-1,3-dioxolan-2-one. Its presence and amounts were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard: MS m/z (%) 102 (M^+, 2), 87 (10), 57 (64), 43 (73), 29 (100). Lit. [8].



Dimethyl carbonate. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR. The spectrum showed the presence of a strong absorptions around 1740 cm^{-1} assigned to carbonyl group of the carbonate. Its presence and amount were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard: MS m/z (%) 90 (M^+ , 10), 57 (100). Lit. [6].

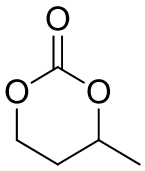


Di(1*H*-imidazol-1-yl)methanone. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR. The spectrum showed the presence of a strong absorptions around 1716 cm^{-1} assigned to carbonyl group. The

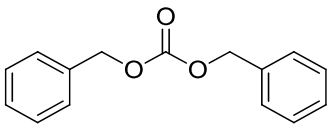


presence and amount of diimidazolyl compound were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard. MS m/z (%) 106 (M^+ , 40), 91 (5), 79(10), 68 (100), 51 (5). Lit. [6].

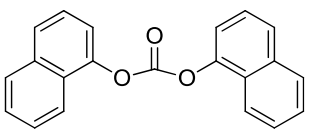
4-methyl-1,3-dioxan-2-one. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR. The spectrum showed the presence of a strong absorptions around 1718 cm^{-1} assigned to carbonyl group. The presence and amount of cyclic carbonate were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard. MS m/z (%) 115 (M^+ , 80), 101 (>2), 86(4), 73 (5), 59 (65), 55(100). Lit. [8]



Dibenzyl carbonate. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR The spectrum showed the presence of a strong absorptions around 1777 cm^{-1} assigned to carbonyl group. The presence and amount of carbonate were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard. Ms m/z (%) 180 [M+- 62] (10); 151 (12); 107 (41); 92 (24); 91 (100); 79 (40); 77 (24); 51 (13). Lit. [9].



Di(naphthalen-1-yl) carbonate. A measured sample of reaction mixture was dissolved in CH_3CN and analyzed by IR. The spectrum showed the presence of a strong absorptions around 1782 cm^{-1} assigned to carbonyl group. The presence and amount of carbonate were ascertained by GC-MS analysis using 4-methyl-anisole as an external standard. MS m/z (%) 314 (M^+ 88); 269 (97); 253 (25); 241 (35); 226 (>5); 165 (>5); 144 (33); 127 (100); 115 (80), 101 (5), 89 (7), 77 (10). Lit. [10].



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