



Journal Name
ARTICLE

Depolymerization of poly-(bisphenol A carbonate) under mild conditions by solvent-free alcoholysis catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene as a recyclable organocatalyst: a route to chemical recycling of waste polycarbonate

Received 00th January 20xx,
Accepted 00th January 20xx

DOI:
10.1039/c7gc02063e

www.rsc.org/

Eugenio Quaranta,* Damiano Sgherza and Giuseppe Tartaro

DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) is an active catalyst of poly-(bisphenol A carbonate) (PC) alcoholysis and promotes selectively and quantitatively the solvent-free (no auxiliary solvent used) depolymerization of the polymeric material to bisphenol A (BPA) and the corresponding organic carbonate (RO)₂CO under not severe conditions (295 K - 373 K). The process is relevant to the chemical recycling and valorization of the waste polymer. Using methanol as the reference alcohol, the influence of a few experimental parameters (temperature, MeOH/PC ratio, DBU load and concentration) on conversion time and products (BPA; dimethyl carbonate (DMC)) yield has been investigated. The catalytic activity of DBU has been compared with that of other organocatalysts such as DABCO (1,4-diazabicyclo[2.2.2]octane) and DMAP (4-(dimethylamino)pyridine), which were found to be less active than the amidine base. The study has been extended to ethanol and EtOH/MeOH mixtures. The ethanolysis reaction afforded BPA and diethyl carbonate (DEC) selectively with high yield, but proceeded more slowly than methanolysis. In MeOH/EtOH solutions the depolymerization afforded, beside BPA, a mixture of DMC, DEC, and methyl ethyl carbonate (MEC): by this way, a mixed carbonate such as MEC was synthesized in one step with satisfactory yields (60%). The recyclability of the catalyst in the depolymerization process has been investigated. At the end of the reaction the catalyst was still active. It can be reused *in situ* by adding more fresh polymer at the end of each catalytic run. As well, DBU can be also recovered from the reaction mixture as a DBU-BPA adduct and effectively reused in a successive run.

Introduction

In the last few decades, chemical recycling of plastics has raised great interest as a useful strategy to reduce the environmental and social impact of this typology of wastes, providing an intriguing alternative to more traditional technological solutions such as landfill disposal, mechanical recycling and energy recovery. This approach, which implies the conversion of waste polymer into valuable chemicals by chemical methods, is noteworthy as it looks at the waste as a potential resource rather than a mere refuse, and responds to the current worldwide need of economizing both carbon and energy and preserving fossil reserves from depletion.¹⁻⁴

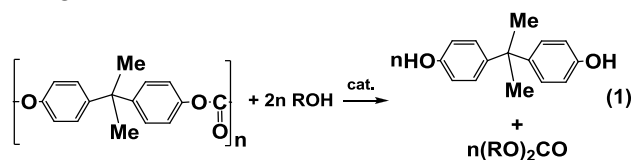
Poly[2,2-bis(4-hydroxyphenyl) propane carbonate] (PC; poly-(bisphenol A carbonate)) is one of the most widely used thermoplastics. Its market is rising steeply and is expected to reach US\$ 19.59 Bn in 2020.⁵⁻⁷ The rise in the utilization of PC calls for the developments of after-use treatments. Chemical recycling may provide a suitable way of valorizing waste PC.

This option aims at regenerating the starting monomer 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), which can be reused to produce new virgin plastic, and/or at obtaining chemicals with added value.

Several routes can be envisaged for recycling waste PC by chemical methods. Pyrolysis shows the main disadvantage of low BPA selectivity due to the large production of by-products.⁸⁻¹⁰ Other options are based on the cleavage of carbonate bond through a chemical reaction¹¹⁻⁴⁹ such as, for instance, hydrolysis,²⁴⁻⁴³ aminolysis,^{22,23} alcoholysis,^{11-16,29,45-48} or also glycolysis.¹⁷⁻²¹ In principle, a few of these approaches not only allow the regeneration of the monomer (BPA), but can also afford useful coproducts, for instance organic carbonates, or carbamates and ureas, if the polymer is reacted, respectively, with alcohols or amines. Carbonic acid diesters, as well as carbamates and ureas, are traditionally synthesized from toxic harmful phosgene and, therefore, the latter methods provide an alternative synthetic route to these products which utilizes waste PC as a safer nontoxic carbonylating agent in place of COCl₂.⁵⁰⁻⁵³

^a Dipartimento di Chimica, Università degli Studi "Aldo Moro" di Bari, Campus Universitario, Via E. Orabona, 4, 70126, Bari, Italy.
E-mail: eugenio.quaranta@uniba.it.

[†]Electronic Supplementary Information (ESI) available: FTIR, NMR, MS, work up of the reaction mixture. See DOI: 10.1039/x0xx00000x



In this work we have focused on the alcoholysis reaction (eqn (1)). In principle, reaction (1) provides an example of a 100% atomically economic process. In fact, depending on the alcohol used, reaction (1) affords, besides BPA, the relevant organic carbonate $(RO)_2CO$ as a useful coproduct.⁵⁴ Relative to other approaches, such as PC pyrolysis or hydrolysis, detailed studies on the alcoholysis of PC are relatively few. The reaction can proceed in neat alcohol (used as depolymerizing agent and solvent; no auxiliary solvent used)^{12,15,16,45-48} but, even in the presence of a catalyst,^{15,47,48} severe experimental conditions are required (high temperatures (493 K);¹⁶ utilization of the alcohol in near critical or supercritical conditions^{12,15,46,47}) because of the poor solubility of PC in the used reaction medium (MeOH, EtOH). Milder conditions have been applied when the alcoholysis reaction (eqn (1); R = Me) has been carried out in a solvent, such as THF, 1,2-dichloroethane, toluene, 1,4-dioxane, N-methyl-2-pyrrolidone, able to dissolve the polymeric material.^{11,29} However, the utilization of an auxiliary solvent as reaction medium is poorly desirable in this ambit because of the impact on waste generation, separation steps, and processing costs. Moreover, the implementation of the above solvents at industrial scale is not so straightforward, especially for those ranked as hazardous (1,2-dichloroethane, 1,4-dioxane, N-methyl-2-pyrrolidone).⁵⁵ hazardous solvents, in fact, put severe constraints on scale-up and their substitution is considered a priority. Inorganic bases (NaOH, for instance) are active catalysts of reaction (1).^{11,15,29} However, the used base cannot be recycled, is wasted at the end of the process, may cause equipment corrosion and generate environmental problems. In the attempt to overcome the above shortcomings ionic liquids have been also explored as reaction media and/or catalysts.^{13,14}

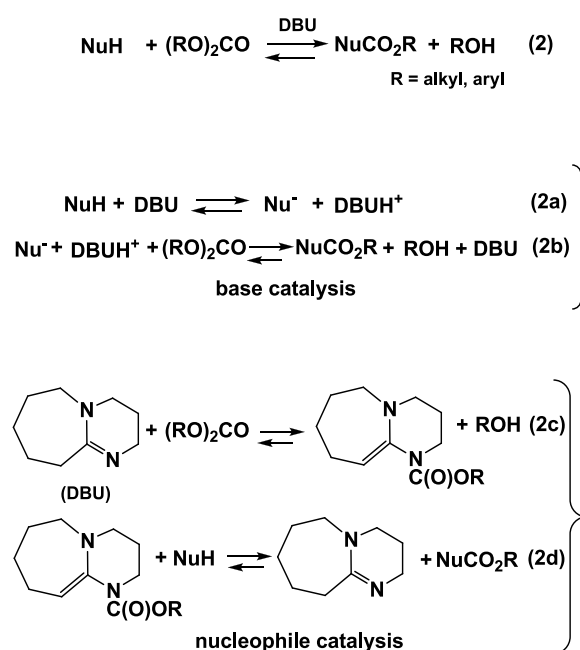
A significant breakthrough in this field may come from the search for new protocols, simpler from the operational standpoint, which exclude the use of auxiliary substances (cosolvents, for instance), avoid harsh reaction conditions, and make use of selective catalytic systems susceptible to be reused. The utilization of organocatalysts still remained unexplored in this ambit. We note that reaction (1) implies the carbonylation of a relatively weak nucleophile ROH by diaryl substituted carbonate groups. Elsewhere we have shown that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can promote the carbonylation of weak nucleophiles NuH (pyrrole and other N-heteroaromatics, for instance) with carbonic acid diesters (eqn (2));⁵⁶⁻⁵⁸ DBU can work both as a base, activating NuH through the formation of the more nucleophilic anion Nu^- (Scheme 1; base catalysis)⁵⁸, and as a nucleophile capable of activating the carbonate group through the formation of a N-carbonyl substituted ketene aminal (Scheme 1; nucleophile catalysis),⁵⁸⁻⁶⁰ which can effectively transfer the CO_2R group to nucleophiles NuH such as N-heteroaromatics (pyrrole) and even alcohols.⁵⁹ These results prompted us to explore DBU as

a potential catalyst of PC alcoholysis. Herein, we fully report on the activity of DBU as the catalyst of reaction (1) and describe a novel simple efficient protocol of PC alcoholysis under mild solvent-free conditions, using the alcohol as reactant and reaction medium and DBU as recyclable catalyst.

Experimental

General methods and materials

In this study pure PC pellets (3 mm length \times 2 mm diameter) were used as a model of waste PC. Polycarbonate used in this work was from Aldrich ($M_w \sim 64000$). Scheme 2 shows the repeating unit (254.29 g/mol) of the polymer and highlights the nature of the additive, 4-(2-phenylpropan-2-yl)phenol (4-cumylphenol; 4-CP), used as a chain-terminator.⁶¹ The molar ratio 4-CP/BPA in the used polymer was equal to 0.035, as determined by NMR.⁴³ DBU (Aldrich) was used as received and manipulated under an inert atmosphere to prevent any contamination from atmospheric CO_2 ⁶² or moisture. Methanol (Carlo Erba) used in methanolysis reactions was previously dried according to conventional methods (over Mg)⁶³ and stored under N_2 . Ethanolysis experiments were carried out in absolute ethanol (Carlo Erba), used as received. GC analyses were performed with a HP 5890 Series II gas-chromatograph (capillary column: Heliflex AT-5, 30 m \times 0.25 mm, 0.25 μm film thickness). GC-MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GC-MS QP5050 selective mass detector (capillary column: Supelco MDN-5S, 30 m \times 0.25 mm, 0.25 μm film thickness). IR spectra were taken on a Shimadzu FTIR Prestige 21 spectrophotometer or a Perkin Elmer Frontier MIR/FIR spectrophotometer equipped with a Pike GladiATR (diamond crystal) accessory. NMR spectra were recorded with a Varian Inova 400 spectrometer or with an Agilent 500 instrument. Chemical shifts are in δ (ppm) vs TMS.



Scheme 1 DBU-promoted carbonylation of nucleophiles NuH with carbonic acid diesters $(RO)_2CO$.

Alcoholysis of poly-(bisphenol A carbonate) in the presence of DBU: general procedure

The alcoholysis reaction was carried out in a ~40 mL glass tube equipped with a Sovirel screw cap and Thorion stopcock. The polycarbonate (~0.5 g), the alcohol (MeOH or EtOH or a MeOH/EtOH mixture) and the catalyst were introduced in sequence into the glass reactor under an inert gas (N₂) stream. The reactor, once charged with the reactants, was dipped into an electrically heated silicon oil bath. The system was stirred at the working temperature until complete conversion of the polymer into the end products (BPA, (RO)₂CO; see, later, Scheme 3), as ascertained by monitoring the reaction mixture by FTIR and GC or GCMS. The reaction solution was then analyzed quantitatively by GC. Toluene and n-heptane were respectively used as internal standards for the GC determination of dimethyl carbonate (DMC) and diethyl carbonate (DEC), except in the experiments carried out with MeOH/EtOH mixtures where the internal standard selected for the GC analysis of the carbonate products was n-dodecane. In those cases wherein BPA yield was determined by GC, biphenyl was used as internal standard for the GC quantitation of this product.

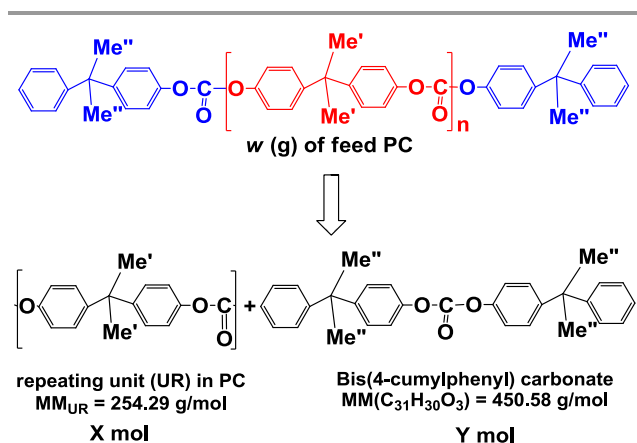
BPA yield was calculated through eqn (3), wherein n_{BPA} are the moles of BPA product determined via GC or isolated and n°_{BPA} are the moles of BPA units incorporated in the mass w of PC feed and calculated through eqn (4),[†] where MM_{UR} (254.28 g/mol) is the molar mass of the repeating unit, $\text{MM}_{\text{bis(4-cumylphenyl) carbonate}}$ (450.58 g/mol) is the molar mass of bis(4-cumylphenyl) carbonate (see also Scheme 2) and 0.035 is the molar ratio 4-CP/BPA in the used polymer.⁴³

$$\text{BPA yield (\%)} = (n_{\text{BPA}}/n^{\circ}_{\text{BPA}}) \times 100 \quad (3)$$

$$n^{\circ}_{\text{BPA}} = w / (\text{MM}_{\text{UR}} + 1/2 \text{MM}_{\text{bis(4-cumylphenyl) carbonate}} \times 0.035) \quad (4)$$

The yield in organic carbonate (RO)₂CO was calculated through eqn (6), wherein $n_{(\text{RO})_2\text{CO}}$ are the moles of organic carbonate determined via GC and n_{CO_3} was calculated according to eqn (5).[†]

$$(\text{RO})_2\text{CO yield (\%)} = (n_{(\text{RO})_2\text{CO}}/n_{\text{CO}_3}) \times 100 \quad (6)$$



Scheme 2 Sketch of the polymeric chain: the repeating unit (UR) and the nature of the species, 4-cumylphenol, used as chain stopping agent in the synthesis of the used polymer have been highlighted. Accordingly, it may be assumed that a mass w (g) of feed PC consists formally of X mol of repeating units (UR) and Y mol of bis(4-cumylphenyl) carbonate (see, later, footnote [†]).

In a few methanolysis experiments stopped before of full depolymerization of PC (*i.e.*, before of disappearance of the PC pellets), the uncovered polymeric material was isolated by filtering the reaction mixture. The filtered solid was washed with MeOH, dried under vacuum, weighted and identified as uncovered polycarbonate through its FTIR spectrum which was identical to that of feed PC (Fig. S1). The PC depolymerization yield was calculated through eqn (7), where w' is the mass of PC recovered.

$$\text{PC depolymerization yield (\%)} = [(w - w')/w] \times 100 \quad (7)$$

Work-up of the reaction mixture

After the complete conversion of the polymer into the end products, the reaction solution was distilled at room temperature in vacuum to separate both the organic carbonate (RO)₂CO and the excess of alcohol, which were quantitatively recovered, free of DBU, by condensation in a cold trap. The solid residue of distillation can be processed by different ways as described below.

Extraction with diethyl ether/H₂O (method A). The residue of distillation can be purified from DBU by extraction with diethyl ether/H₂O. The organic phase was then dried on MgSO₄, filtered and evaporated in vacuum to give a DBU-free residue containing BPA and 4-CP (Fig. S2). Indicating with w'' the mass of the isolated mixture (BPA plus 4-CP), the overall (BPA + 4-CP) yield (~91%) can be calculated through equation (8).

$$\text{Yield}_{(\text{BPA} + 4\text{-CP})} = w'' / (n^{\circ}_{\text{BPA}} \times \text{MM}_{\text{BPA}} + n^{\circ}_{4\text{-CP}} \times \text{MM}_{4\text{-CP}}) \quad (8)^{\dagger}$$

The aqueous phase was evaporated in vacuum under gentle warming to afford a colorless oil. The GCMS analysis of the oil showed that DBU passed into the aqueous phase together with some BPA (Fig. S3).

The DBU-containing oily residue can be directly recycled in a successive catalytic run after addition of fresh methanol and more PC (see, later, Table 6).

Washing with diethyl ether (Method B). According to an alternative procedure the residue of distillation can be purified from DBU by washing the solid material with diethyl ether (20 mL). The resulting suspension was filtered and the ethereal phase was evaporated in vacuum to give a DBU-free residue (Fig. S4 and S5) containing BPA and 4-CP (typically 70-75 % yield, calculated through eqn (8)). The solid insoluble in ether was dried in vacuum and characterized spectroscopically (IR, ¹H and ¹³C NMR; Fig. S6-S10). The ¹H NMR analysis (see Chart 1 for atom numbering) showed that it was a BPA-DBU adduct (BPA/DBU molar ratio equal to 2.5 mol/mol).

FT-IR (nujol): 3267 (v br), 1643 (ms), 1610 (m), 1593 (m), 1506, 1323, 1247, 1228, 1175, 1101, 1080, 1012, 831, 761, 723 cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): the resonances of BPA were found at δ 1.51 (Me), 6.60 (dm, 8.6 Hz, H3) and 6.95 (dm, 8.5 Hz, H2) ppm, while the signals of DBU were easily distinguishable at δ 1.4-1.6 (overlapped multiplets, H3,H4,H5), 1.70 (quint, 6 Hz, H10), 2.34 (m, H6), 3.10 (t, H9), 3.19-3.23 ppm (overlapped multiplets, H2 and H11). The OH protons

ARTICLE

were responsible of a very broad hardly detectable signal around 8 ppm.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): the ^{13}C spectrum displayed the signals of BPA at δ 30.87 (Me), 40.83 (CMe_2), 114.60 (C3), 127.18 (C2), 140.60 (C1), 155.36 ppm (C4), while the resonances of DBU were located at δ 21.55 (C10), 25.24, 27.59, 28.84 (C3, C4, C5), 34.98 (C6), 41.99 (C9), 47.53, 52.06 (C2 and C11), 161.27 ppm (C7).

^1H NMR (500 MHz, CD_3OD): the resonances of BPA were found at δ 1.55 (Me), 6.62 (dm, 8.8 Hz, H3) and 6.98 (dm, 8.3 Hz, H2) ppm, while the signals of DBU were easily distinguishable at δ 1.68-1.80 (overlapped multiplets, H3, H4, H5), 2.00 (quint, 5.9 Hz, H10), 2.63 (m, H6), 3.31 (partially overlapped to the residual signal of solvent, H9), 3.50 (t, 6 Hz, H11), 3.56 ppm (multiplet, H2).

^{13}C NMR (125 MHz, CD_3OD): the ^{13}C spectrum displayed the signals of BPA at δ 31.73 (Me), 42.38 (CMe_2), 115.99 (C3), 128.64 (C2), 142.69 (C1), 157.29 ppm (C4), while the resonances of DBU were located at δ 20.57 (C10), 25.03, 27.57, 29.99 (C3-C5), 33.89 (C6), 39.64 (C9), 49.45, 55.25 (C2 and C11), 167.20 ppm (C7).

The adduct, once dried under vacuum, was ready to be recycled in a successive catalytic run after addition of fresh methanol and more PC (see, later, Table 7).

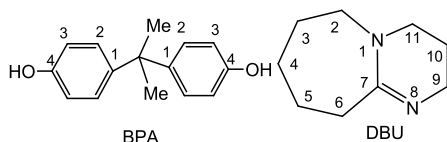


Chart 1 Atom numbering in BPA and DBU.

Isolation of pure BPA. BPA and 4-CP can be isolated as a pure compounds by fractionating the residue of distillation on a silica gel column, using, as eluent, petroleum ether/ethyl acetate 6:1 (v/v) until elution of 4-CP and, afterwards, petroleum ether/ethyl acetate 2:1 (v/v). BPA yield: 91-93% (Fig. S11 and S12); 4-CP yield: 95% (Fig. S13 and S14).

Results and Discussion

Methanolysis of poly-(bisphenol A carbonate) in the presence of DBU

In this work methanol was selected as the reference alcohol. The alcohol was used both as depolymerizing reagent and solvent despite the very poor solubility of the polymer in this reaction medium. The methanolysis reaction (eqn (1), $\text{R} = \text{Me}$) provides a potential way to obtain, in addition to BPA, also DMC as a useful coproduct. Nowadays, DMC is receiving great attention not only as a green solvent, but also as a safe nontoxic reagent, being used as succedaneous for phosgene in carbonylation reactions and as a methylating agent in place of harmful dimethylsulfate and methyl halides.^{50,52,64}

A few preliminary tests, carried out with a stoichiometric amount of DBU ($\text{mol}_{\text{DBU}}/\text{mol}_{\text{CO}_3} \sim 1$), showed that the amidine superbase can promote the methanolysis of PC even at ambient temperature (Fig. 1 and Table 1). However, under the

working conditions, the alcoholysis reaction proceeded slowly with very long conversion times, even when the concentration of DBU was increased markedly (Fig. 1, curve c; Table 1, entry 3). The reaction was by far faster at higher temperature. At 343 K, in fact, under conditions otherwise comparable with those used at 295 K (entry 3, Table 1), the conversion of PC into BPA and DMC was achieved in little more than half an hour (entry 4, Table 1).

Consequently, the methanolysis reaction was investigated at temperatures higher than 295 K under conditions more appealing from an applicative standpoint implying the use of a catalytic amount of DBU. Fig. 2 compares the results obtained at 343 K and 373 K using a DBU load around 6% (m/m), corresponding to 10 mol%.[‡] At 373 K, the full depolymerization of the polycarbonate, monitored by following the disappearance of the PC pellets, was attained in ~ 30 min, and after this time both DMC and BPA were obtained in quantitative yield ($\sim 99\%$, by GC).[¶]

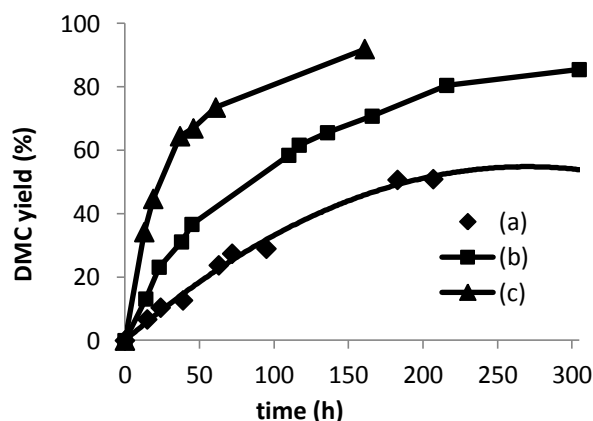


Fig. 1 PC methanolysis in the presence of a stoichiometric amount of DBU ($\text{mol}_{\text{DBU}}/\text{mol}_{\text{CO}_3} \sim 1$), at 295 K. (a) PC: 0.174 g; MeOH/PC : 23 $\text{m}_{\text{MeOH}}/\text{m}_{\text{PC}}$, 183 $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_3}$; DBU concentration: 0.021 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$. (b) PC: 0.5017 g; MeOH/PC : 7.9 $\text{m}_{\text{MeOH}}/\text{m}_{\text{PC}}$, 64 $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_3}$; DBU concentration: 0.060 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$. (c) PC: 0.5011 g; MeOH/PC : 2.5 $\text{m}_{\text{MeOH}}/\text{m}_{\text{PC}}$, 20 $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_3}$; DBU concentration: 0.19 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$.

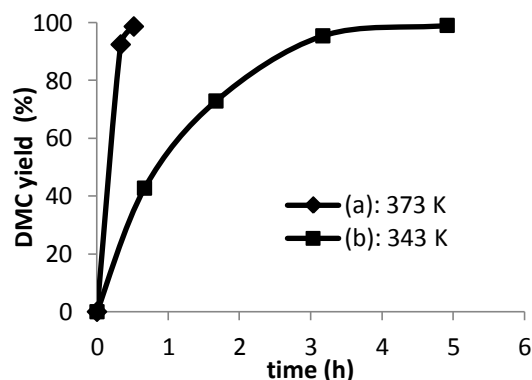


Fig. 2 PC methanolysis in the presence of a catalytic amount of DBU at (a) 373 K and (b) 343 K. (a) PC: 0.51135 g; MeOH/PC : 4.6 $\text{m}_{\text{MeOH}}/\text{m}_{\text{PC}}$, 37 $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_3}$; DBU concentration: 0.0095 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$; DBU load: 5.6% m/m, 9.4 mol%. (b) PC: 0.4994 g; MeOH/PC : 4.7 $\text{m}_{\text{MeOH}}/\text{m}_{\text{PC}}$, 38 $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_3}$; DBU concentration: 0.0098 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$; DBU load: 5.9% m/m, 10 mol%.

Table 1 PC methanolysis in the presence of a stoichiometric amount of DBU (DBU/PC: ~ 1 mol_{DBU}/mol_{CO₂})

Entry	PC (g)	MeOH/PC (m _{MeOH} /m _{PC}) (mol _{MeOH} /mol _{CO₂})	DBU concentration (g _{DBU} /mL _{MeOH})	T (K)	t ^a (h)	PC depolymerization (%)	DMC yield ^b (%)	BPA yield ^b (%)
1	0.174	23 183	0.021	295	207	^c	51	^c
2	0.5017	7.9 64	0.060	295	305	87 ^d	85	86
3	0.5011	2.5 20	0.19	295	161	^e	92	95
4	0.496	2.6 21	0.19	343	0.63	100	>99	^c

^a Reaction time. ^b By GC. ^c Not determined. ^d The ATR-FTIR spectrum of the recovered polycarbonate showed no differences with respect to that of the fresh polymer (Fig. S1). ^e Practically quantitative.

Table 2 DBU-catalyzed methanolysis of PC at 373 K: influence of DBU concentration

Entry	PC (g)	MeOH/PC (m _{MeOH} /m _{PC}) (mol _{MeOH} /mol _{CO₂})	DBU concentration (g _{DBU} /mL _{MeOH})	DBU load (%; m/m) (mol%)	t ^a (h)	DMC yield ^b (%)	Notes
1	0.496	46 372	0.0010	5.9 10	1.83	~99	^c
2	0.50150	24 190	0.0020	6.1 10.3	1.5	~99	-
3	0.4947	9.6 77	0.0051	6.2 10.4	0.83	99	-
4	0.51135	4.6 37	0.0095	5.6 9.4	0.52	99	^{d,e}

^a Reaction time. At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^b By GC. ^c Yield_(BPA + 4-CP) = 90% (isolated according to method A, Experimental). ^d BPA GC yield = 99%. ^e See also footnote (¶).

Table 3 DBU-catalyzed methanolysis of PC at 373 K: influence of DBU load

Entry	PC (g)	MeOH/PC (m _{MeOH} /m _{PC}) (mol _{MeOH} /mol _{CO₂})	DBU concentration (g _{DBU} /mL _{MeOH})	DBU load (%; m/m) (mol%)	t ^a (h)	DMC yield ^b (%)	Yield _(BPA + 4-CP) ^c (%)
1	0.496	46 372	0.0010	5.9 10	1.83	~99	90
2	0.503	24 190	0.0010	3.0 5.1	2.25	~99	91
3	0.4928	4.8 39	0.0010	0.6 1.1	6	99	91

^a Reaction time. At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^b By GC. ^c Isolated according to method A (Experimental).

Therefore, the study was continued at 373 K by investigating the influence of a few other parameters (MeOH/PC ratio, DBU concentration, catalyst load) on times and yields of the process. Table 2 summarizes the results obtained when, keeping constant the catalyst load (~6% (m/m); ~10 mol%), the DBU concentration was progressively augmented. The depolymerization process was markedly faster at the highest concentration (entry 4, Table 2), but, as shown in Fig. 3, the diminution of the depolymerization time was more and more moderate as the concentration of DBU increased. Table 3 illustrates the influence of DBU load when keeping constant its concentration (1 mg_{DBU}/mL_{MeOH}). The conversion times lengthened with reducing the catalyst loading.

Nevertheless, even reducing the catalyst load to 1 mol% (entry 3, Table 3), the increase of the conversion time can be contained within reasonable limits (~6 h).

The above data allow to explain the effect of the MeOH/PC ratio on the reaction time required for the full depolymerization of the polymer (~0.5 g). Curve a in Fig. 4 shows that, keeping constant the DBU load (10 mol%), the higher the MeOH/PC ratio the longer the depolymerization time, because of the progressively lower and lower catalyst concentration used in the catalytic runs. On the other hand, curve b in Fig. 4 highlights that, keeping constant the DBU concentration (1 mg_{DBU}/mL_{MeOH}), the time required for the quantitative depolymerization of polycarbonate reduces

Table 4 DBU-catalyzed methanolysis of PC at 373 K: conversion times and yields under different experimental conditions

Entry	PC (g)	MeOH/PC ($m_{\text{MeOH}}/m_{\text{PC}}$) ($\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_2}$)	DBU concentration ($\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$)	DBU load (%; m/m) (mol%)	t^a (min)	DMC yield ^b (%)	Notes
1	0.4932	4.8	0.0051	3.1	95	~99	^c
2	0.4947	9.6	0.0051	5.2	50	99	-
3	0.51135	4.6	0.0095	6.2	32	99	^d
4	0.508	4.7	0.010	9.4	34	99	^e
5	0.502	4.7	0.010	10	32	^f	^g
6	0.51105	4.6	0.010	10.3	35	>99	^h
7	0.499	4.8	0.020	10	20	>99	ⁱ
		38		20.7			

^a Reaction time. At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^b By GC. ^c Yield_(BPA+4-CP) = 90%, isolated according to method A (Experimental). ^d BPA GC yield: 99%. ^e BPA and 4-CP were isolated by column chromatography with yield of 93% and 95%, respectively. ^f Not determined. ^g Yield_(BPA+4-CP) = 91%, isolated according to method A (Experimental). The DBU-containing oily residue isolated from the aqueous phase was analyzed by ¹H and ¹³C NMR. The NMR analysis showed the presence of more BPA (the molar ratio BPA/DBU was found to be equal to 0.5 mol/mol, by ¹H NMR). ^h Yield_(BPA+4-CP) = 75%, isolated according to method B (Experimental). More BPA was recovered as BPA/DBU adduct (mass of the adduct: 137 mg; BPA/DBU molar ratio = 2.5 mol/mol). ⁱ BPA yield = 91% (isolated by column chromatography).

markedly with raising the MeOH/PC ratio as a result of the progressively higher and higher catalyst load used in each experiment. At 373 K, a depolymerization time as short as ~0.5 h was attained using a MeOH/PC ratio around 4.6 (m/m) and working with load and concentration of catalyst equal, respectively, to 10 mol% and 10 mg_{DBU}/mL_{MeOH}. Under the above conditions (see also entries 3 to 6, Table 4), both BPA and DMC formed selectively in practically quantitative yield. A further increase of both catalyst concentration (0.020 g_{DBU}/mL_{MeOH}) and DBU load (~21 mol%) resulted in a further diminution of the reaction time but of only moderate extent (entry 7, Table 4).

The methanolysis reaction was selective as the analysis of reaction mixture did not show, besides DMC, BPA and 4-CP,

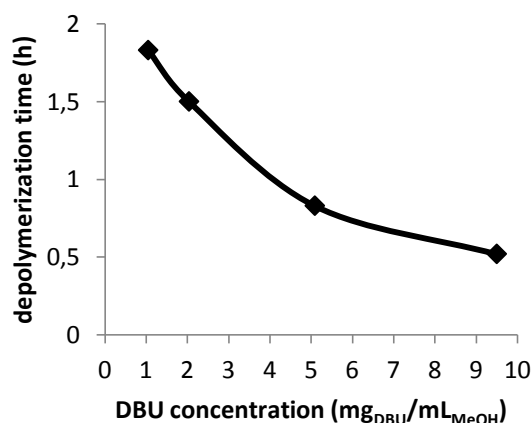


Fig. 3 DBU-catalyzed methanolysis of PC: influence of DBU concentration on the depolymerization time. PC: ~0.5 g; DBU load: ~6% (m/m), ~10 mol%; T: 373 K; see also Table 2

any significant formation of side-products. Methylation products of BPA, which in principle may form from BPA and DMC in the presence of DBU,⁶⁵ or other species, such as PhOH and 4-isopropenylphenol, which may generate from cleavage of BPA propylidene bridge^{66,67} under DBU catalysis, formed, if any, only in trace amounts.

The GCMS analysis of the reaction mixture showed the formation of the species **1a** and **2a** (Chart 2), which are,

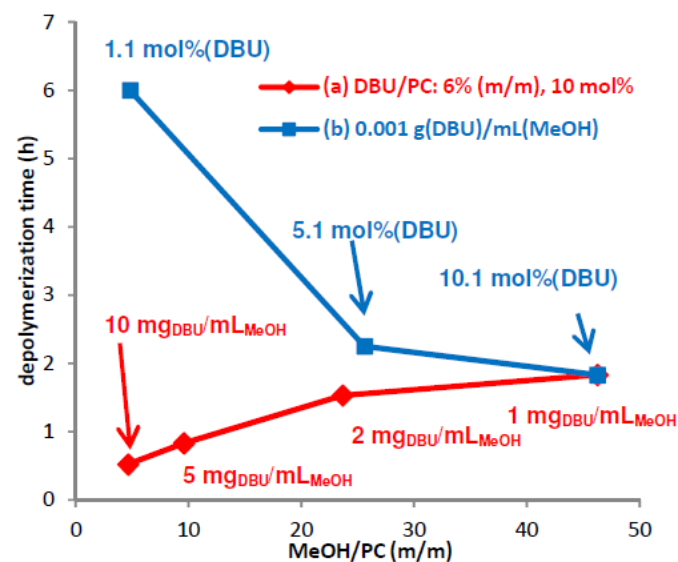


Fig. 4 DBU-catalyzed methanolysis of PC at 373 K: influence of MeOH/PC ratio on the depolymerization time of a fixed amount of polycarbonate (~0.5 g) at (a) constant DBU load (the amount of DBU used in each run was kept constant (0.030 mL) while increasing the volume of MeOH used in each experiment); (b) constant concentration of DBU (the amount of DBU used in each run was proportionally increased with increasing the volume of MeOH used in each experiment).

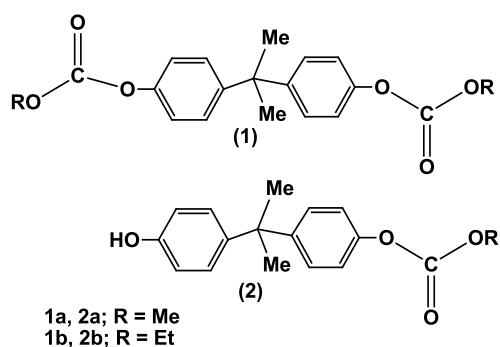
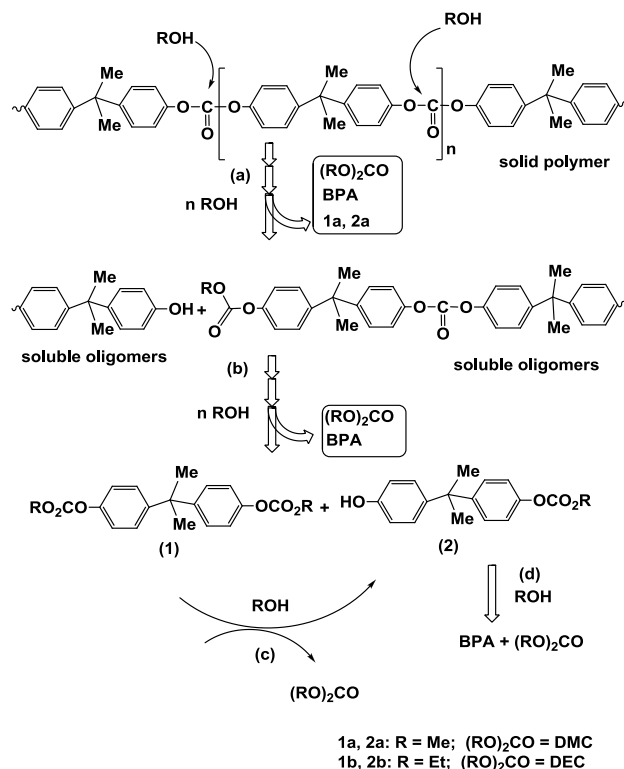


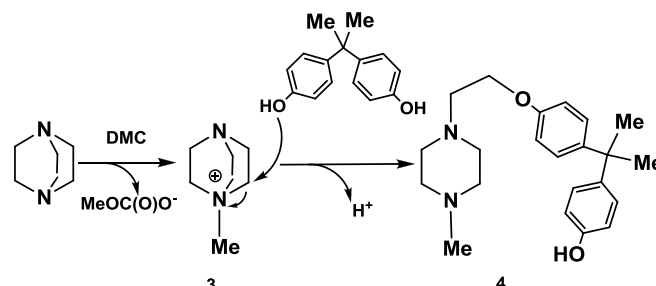
Chart 2 Bis(alkylcarbonate) and mono(alkylcarbonate) of BPA (1 and 2, respectively).

respectively, the bis(methylcarbonate) and the mono(methylcarbonate) of BPA (Fig. S15 and S16). In principle, both **1a** and **2a** might generate since the first steps (step a, Scheme 3) of the alcoholysis process, during which the insoluble solid polymer mainly fragments into smaller soluble oligomers under the attack of the alcohol molecules.¹⁶ The formation of **1a** and **2a** may also accompany the fragmentation of soluble oligomers into smaller and smaller oligomeric species (step b in Scheme 3). However, both **1a** and **2a** can also react with the alcohol and, by this way, can generate DMC and liberate BPA (steps c and d in Scheme 3). **1a** and **2a** have been detected by GC or GCMS always in low to trace amounts depending on the working conditions (reaction temperature, DBU load and concentration). Moreover, the FTIR spectrum of the reaction mixture measured when the depolymerization of PC was still incomplete, or also soon after the disappearance of the PC pellets, did not show evidences of carbonyl absorptions ($\nu_{C=O}$) besides the band at 1757 cm^{-1} due to DMC. The absence of bands at wavenumbers higher than 1757 cm^{-1} , where methyl-aryl-carbonate species, like **1a** and **2a**, and diaryl-carbonate species, like the soluble oligomers generated in the depolymerization process, are expected to absorb,⁵ further confirms that neither **1a** nor **2a** accumulate significantly in the reaction mixture and rules out the presence of soluble oligomers (Scheme 3) in solution at appreciable concentration. These facts suggest, respectively, that (i), under the working conditions, both **1a** and **2a** react easily with methanol to give the final products (steps c and d, Scheme 3), and (ii) the conversion of soluble oligomers into **1a**, **2a**, BPA (step b, Scheme 3) is a relatively faster process than their formation from the starting solid polymer or unsoluble oligomers (step a, Scheme 3). This explain why reaction (1) (R = Me, cat. = DBU) was found to be practically complete when the solid polymer was no longer visible in the reaction mixture (disappearance of the PC pellets) and a homogeneous system was obtained.

The study has been extended to other organocatalysts, such as DABCO (1,4-diazabicyclo[2.2.2]octane) and DMAP (4-(dimethylamino)pyridine) (Table 5). DABCO was less active than DBU, as indicated by the significant longer time required for the complete depolymerization of PC (entry 2, Table 5). The ^1H NMR (500 MHz, CD_3OD) analysis of the reaction mixture at the end of the catalytic run (after evaporation in vacuum of



Scheme 3 Depolymerization of PC by alcoholysis: formation of BPA, $(\text{RO})_2\text{CO}$, 1 and 2.



Scheme 4 DABCO-promoted methanolysis of PC: decomposition of the catalyst.

MeOH) showed, among the various signals, the resonances of 1-methyl-1,4-diazabicyclo[2.2.2]octan-1-ium cation (**3**) at 2.97 (s), 3.14 (t) and 3.27 ppm (t) in addition to the singlet of DABCO at 2.79 ppm.⁶⁹ The formation of **3** implies the methylation of one of the N-atoms of the base, most likely by DMC,⁷⁰ and proves that the catalyst decomposes under the working conditions (Scheme 4). A significant part of the catalyst is involved in the decomposition process as suggested by the value of the molar ratio **3**/DABCO (0.6 mol/mol) determined by ^1H NMR. The GCMS analysis of the reaction mixture showed, besides DMC, 4-CP and BPA, the presence of minor amounts of BPA methylated derivatives (m/z 242) and traces of a species identified as the piperazine derivative **4** (Scheme 4) on the basis of its MS spectrum.^{**} **4** may form from cation **3** by nucleophilic attack of BPA to one of the carbons in α position at the methylated nitrogen with subsequent opening of the relevant ring (Scheme 4).⁶⁹ DMAP was the least active of the organocatalysts investigated. In the presence of DMAP the depolymerization of the solid

Table 5 Methanolysis of PC at 373 K promoted by different organocatalysts

Entry	catalyst	PC (g)	MeOH/PC ($m_{\text{MeOH}}/m_{\text{PC}}$) ($\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_2}$)	catalyst concentration ($\text{mmol}_{\text{catalyst}}/\text{mL}_{\text{MeOH}}$)	catalyst load (mol%)	t^a (h)	DMC ^b (%)	BPA ^b (%)
1	DBU	0.511	4.6 37	0.062	9.4	0.52	99	99
2	DABCO	0.497	4.8 38	0.071	11	2.0	94	96
3	DMAP	0.497	4.8 38	0.065	10	2.3	96 ^c	97 ^c

^a At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^b GC yield. ^c Yield measured after an overall reaction time of 3.25 h (see also main text).

polymer (disappearance of the polymer pellets) to afford a fully homogeneous reaction mixture was achieved only after 2.3 h, and the quantitative conversion of intermediate species such as, for instance, **1a** and **2a**, into the final products (Scheme 3) required a further prolongation of the reaction time, up to a total time of 3.25 h (Table 5). Also in this case the formation of BPA was accompanied by minor amounts of methylated BPA (m/z 242).

Methanolysis of poly-(bisphenol A carbonate) promoted by DBU: isolation of the products, recovery and recycling of the catalyst.

DMC, together with the excess of alcohol, can be recovered by distillation in vacuum at room temperature. The analysis of distillate did not show the presence of DBU, which, therefore, remained quantitatively in the residue of distillation together with BPA and 4-CP. BPA and 4-CP can be isolated as pure compounds in high yield (entry 4 and 7, Table 4) by fractionating the residue of distillation by chromatography on a silica gel column.

However, BPA and 4-CP can be isolated also as a mixture free of DBU (Fig. S2) by extracting the residue of distillation with diethyl ether/water (method A, Experimental; yield_(BPA + 4-CP) ~ 91%). DBU passed into the aqueous phase from which it can be recovered by removing the solvent (H₂O) under vacuum and gently heating. The oil isolated by this way contained not only DBU but also BPA and minor amounts of the product of hydrolysis of DBU **5** [1-(3-aminopropyl)azepan-2-one] (Chart 3), identified by GC-MS (170 m/z) (Fig. S3).

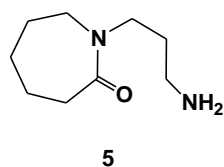
**Chart 3** 1-(3-aminopropyl)azepan-2-one (**5**)

Table 6 shows that the oily residue isolated from the aqueous phase can be directly recycled in a successive run. The overall procedure, however, displays a few drawbacks. In fact, removal of water is both an energy- and time-consuming tedious step, during which some decomposition of the catalyst to **5** (see above) may occur. Moreover, residual amounts of

Table 6 Recycling of DBU (isolated according to method A, Experimental)^a

cycle	t^b (min)	DMC GC-yield (%)	Yield _(BPA + 4-CP) ^c (%)
1	33	>99	92 ^d
2 ^e	42	96	98
3 ^e	75	86	96

^a Experimental conditions. T: 373 K; PC: ~0.5 g; MeOH: 3 mL, $m_{\text{MeOH}}/m_{\text{PC}}$: ~4.8, $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_2}$: ~39; amount of DBU used in cycle 1: 0.030 mL, 0.010 g_{DBU}/mL_{MeOH}; DBU load: 6.0% (m/m), 10 mol%. ^b Reaction time. At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^c See eqn (8). ^d More BPA passed into the aqueous layer together with DBU during the extraction process and was recycled with DBU in the successive run. ^e DBU was recycled not as a pure compound, but as an oil containing BPA coming from the previous cycle.

water in the recycled catalyst can open the way to the PC hydrolysis side-reaction with formation of BPA and CO₂ and consequent diminution of DMC selectivity (in Table 6, compare DMC yield in cycles 2 and 3 with that in cycle 1). Finally, CO₂ formed through the hydrolysis reaction may cause the deactivation of part of the catalyst through the formation of DBUH⁺ carbonate salts. These facts, as well as the losses of DBU intrinsically related with the adopted isolation procedure, may explain why the time required for the full depolymerization of PC becomes rapidly longer and longer as the number of cycles increases (Table 6).

Therefore, an alternative more straightforward method was developed for isolating the BPA/4-CP mixture and recovering DBU more effectively (method B, Experimental). The solid residue obtained by distillation was washed with diethyl ether. As ascertained by NMR, this procedure allowed to isolate most of BPA and 4-CP (Table 4, Entry 6) free of the amidine base (Fig. S4 and S5), while DBU was recovered quantitatively not as a pure compound but as a BPA-DBU adduct, poorly soluble in diethyl ether. Typically, the molar ratio BPA/DBU in the adduct was found, by ¹H NMR, to be equal or, in a few cases, close to 2.5 mol/mol. This can explain the lower yield_(BPA + 4-CP) obtained in this case (Table 4, Entry 6). The FTIR spectrum of the adduct (Fig. S6) showed, besides the predominant absorptions due to BPA, an absorption at 1643 cm⁻¹ ascribable to the presence of DBUH⁺ cation which can form through a proton transfer reaction between BPA and DBU.^{††} As a whole, these facts

suggest that, in the adduct, deprotonated BPA molecules (most likely $\text{HOC}_6\text{H}_4\text{-C}(\text{Me})_2\text{-C}_6\text{H}_4\text{O}^-$ monoanions) as well as intact BPA molecules coexist all together, probably engaged within a network of intermolecular H-bonds including, most likely, also DBUH^+ cations. Unfortunately, to date, a more detailed description of this compound in the solid state has been prevented by our failure in obtaining crystals of the adduct suitable for X-ray diffraction analysis. The adduct has been fully characterized in solution (CD_3OD , DMSO-d_6) by ^1H and ^{13}C NMR (Experimental and Fig. S7-S10). The comparison with the NMR spectra of BPA, DBU and DBUHCl in the same solvents (CD_3OD , DMSO-d_6) indicates that the signals observed in the spectra of the adduct are, actually, averaged resonances due, respectively, to the systems $\text{HOC}_6\text{H}_4\text{-C}(\text{Me})_2\text{-C}_6\text{H}_4\text{OH}/\text{HOC}_6\text{H}_4\text{-C}(\text{Me})_2\text{-C}_6\text{H}_4\text{O}^-$ and DBU/DBUH^+ , as a result of a fast (on the ^1H and ^{13}C NMR timescales) proton exchange according to equilibrium (9). The direction of the shifts observed for the ^1H and ^{13}C resonances assigned to the system DBU/DBUH^+ is that expected from the comparison with the resonances of DBU and DBUH^+ in the solvents used (CD_3OD , DMSO-d_6 ; Fig. S17-S20). Only a few of the resonances assigned to BPA in the NMR spectra (^1H , ^{13}C) of the adduct exhibit an appreciable shift with respect to those measured for the pure compound in pure CD_3OD ⁴³ or DMSO-d_6 (Fig. S11-S12) (see, for instance, the signals due to carbons C1, C3 and C4). A relatively larger downfield shift (+0.5 ppm in DMSO-d_6 ; +1.4 ppm in CD_3OD) was observed for the resonance assigned to C4, as expected if the OH group directly bound to this carbon is deprotonated.^{††}

The recyclability of the adduct in the depolymerization reaction has been explored. The adduct, once isolated, can be directly reused in a successive run (Table 7). The moderately longer conversion times measured in the recycling experiments may be ascribed not only to unavoidable minor losses of adduct during the isolation workup, but may also reflect a lower activity of the adduct relative to fresh DBU (see, later, footnote⁵⁵). Nevertheless, even after 7 cycles both the productivity and selectivity of the process maintained very high. No evidence of catalyst decomposition was observed with increasing the number of cycles. Moreover, the catalyst recovered from the last run (Table 7) exhibited spectroscopic features analogous to those of the catalyst recovered from the first cycle.

However, the catalyst can be reutilized also *in situ* by simply adding more fresh PC at the end of each run, soon after the full depolymerization of the formerly feed polymer. The depolymerization process, which was followed by monitoring the formation of DMC by GC (Fig. 5), started again after each addition of fresh polycarbonate in accordance with the fact that the catalyst was still active at the end of each catalytic run. DMC total yield was practically quantitative after each cycle (curve b, Fig. 6). Also BPA can be isolated together with 4-CP (method A; Experimental) in high yield ($\text{yield}_{(\text{BPA} + 4\text{-CP})} = 90\%$) at the end of the last cycle. Nevertheless, the depolymerization process became slower and slower after each addition of fresh PC (Fig. 5) as a result of the fact that the

activity of the catalyst decreased after each cycle. The effect is clearly illustrated in Fig. 6, showing that (i) the duration of each cycle increased with the number of cycles (curve a), and

Table 7 Recycling of DBU (isolated according to method B, Experimental)^a

cycle	t^b (min)	DMC GC yield (%)	Yield _(BPA + 4-CP) ^c (%)
1	34	>99	73
2	42	99	98
3	46	98	98
4	49	99	98
5	51	98	98
6	52	99	97
7	53	98	98

^a Experimental conditions. T: 373 K; PC: ~0.5 g; MeOH: 3 mL, $m_{\text{MeOH}}/m_{\text{PC}}$: ~5, $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_2}$: ~39; amount of DBU used in cycle 1: 0.030 mL, 0.010 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$, DBU load: 6% (m/m), 10 mol%. After each run DBU was recovered as adduct with BPA (see main text) and reused in the successive cycle. ^b Reaction time. At that time the depolymerization of the solid polymer was quantitative (disappearance of the pellets of PC) and a homogeneous reaction mixture was obtained. ^c See eqn (8).

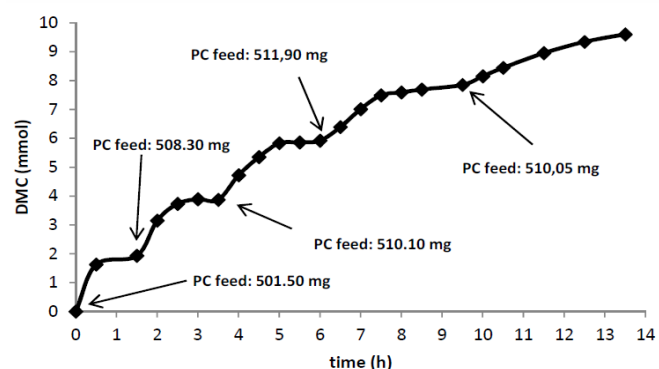


Fig. 5 DBU-promoted methanolysis of PC: *in situ* reutilization of the catalyst. Curve of formation of DMC. T: 373 K; PC feed in each cycle: ~0.5 g; MeOH: 15 mL, $m_{\text{MeOH}}/m_{\text{PC}}$: 24, $\text{mol}_{\text{MeOH}}/\text{mol}_{\text{CO}_2}$: ~190; DBU: 0.030 mL, 0.0020 $\text{g}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$, DBU load: ~6% (m/m), ~10 mol%.

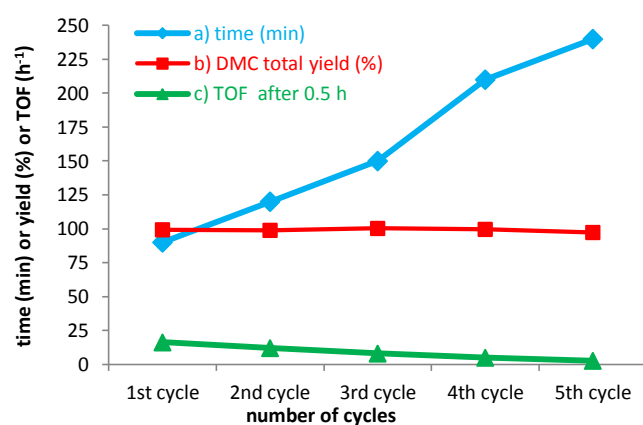


Fig. 6 DBU-promoted methanolysis of PC: *in situ* reutilization of the catalyst (see the legend of Fig. 5 for the experimental conditions). (a) Duration of each cycle (min). (b) Total yield (%) of DMC at the end of each cycle. (c) Turnover frequency (h^{-1}) measured for each cycle after a reaction time of 0.5 h.



Journal Name
ARTICLE

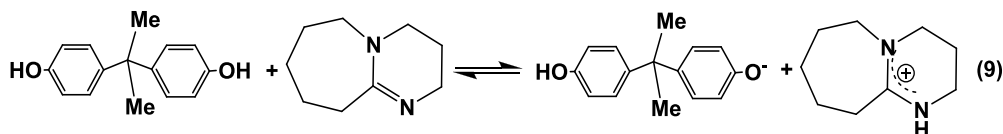


Table 8 DBU promoted alcoholysis of PC: ethanolysis vs methanolysis ^a

entry	PC (mg)	MeOH (mL) (mmol)	EtOH (mL) (mmol)	<i>t</i> ^b (h)	PC conversion (%)	DMC ^c (%)	MEC ^c (%)	DEC ^c (%)	BPA yield (%)
1	508	3.0 74	-	0.57	100	99	-	-	93 ^d
2	495	1.25 31	1.80 31	1.25	100	50	45	4	91 ^d
3	504	0.55 14	2.45 42	1.32	100	26	60	13	97 ^c
4	501	0.40 9.9	2.6 45	1.55	100	19	52	28	97 ^c
5	501	0.135 3.3	2.9 49	2.48	100	5	34	60	95 ^c
6	511.45	-	3.0 51	3.25	100	-	-	98	92 ^e

^a T: 373 K; DBU: 0.030 mL; DBU load: ~6% (m/m), ~10 mol%. ^b Reaction time (see also main text). ^c GC yield. ^d Isolated as pure compound by column chromatography. ^e Yield_(BPA + 4-CP); isolated according to method A (Experimental).

(ii) the TOF measured at 0.5 h markedly decreased after 5 cycles (curve c). The observed diminution of catalytic activity can be related to the progressive increase of BPA concentration in the reaction mixture as the number of cycles increased. In fact, according to reaction (9), the higher the concentration of BPA the lower is the concentration of free DBU in the reaction medium as a result of the fact that the position of equilibrium (9) moves more and more to the right.⁵⁵

DBU-promoted ethanolysis of PC

The alcoholysis protocol described above has been extended also to a safer less volatile alcohol than methanol, such as ethanol. In principle, PC ethanolysis, besides generating BPA, can provide a synthetic entry into diethyl carbonate (DEC), currently synthesized through phosgenation methods. DEC is a well-known linear organic carbonate which finds wide applications in several fields, being used, for instance, as a fuel additive, component of electrolytes for lithium ion batteries and starting material for the production of polycarbonates.⁷¹

Poly-(bisphenol A carbonate) is poorly soluble in ethanol. To the best of our knowledge, PC ethanolysis has been investigated under severe conditions of temperature and pressure (for instance: 563 K, 8.5 MPa), using sub- or supercritical ethanol as reagent and solvent.^{12,46,47} As an example, at 563 K, in the absence of any catalyst, PC was

degraded by ethanol into DEC and BPA with yields, respectively, of 89% and 90% after 50 min.¹²

Entry 6 in Table 8 shows that in ethanol, without using any auxiliary solvent, PC can be depolymerized in the presence of DBU under much milder conditions (373 K). DEC was obtained in practically quantitative yield within 3.25 h. Also BPA was

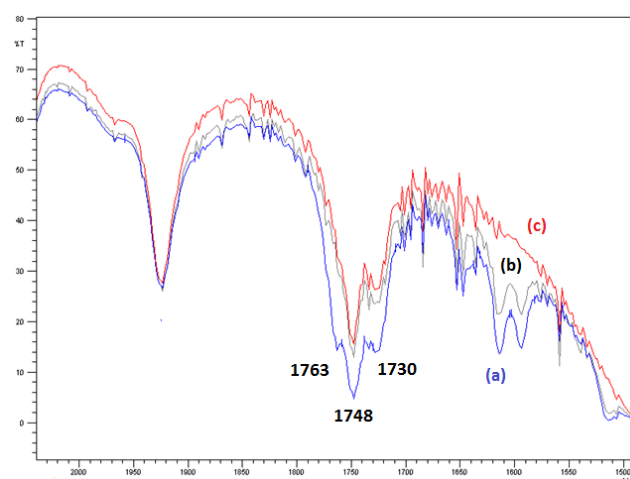


Fig. 7 DBU promoted ethanolysis of PC. Experimental conditions: see entry 6 in Table 8. (a) FTIR spectrum of the reaction solution after 1 h (soon after the disappearance of the pellets of polymer). (b) FTIR spectrum of the reaction solution after 3.25 h, at the end of the catalytic run (after complete conversion of **1b** and **2b**). (c) FTIR spectrum of diethyl carbonate in ethanol.

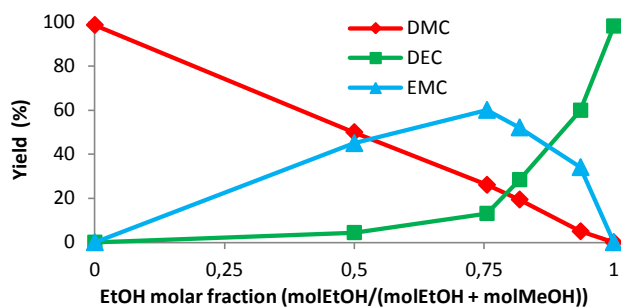


Fig. 8 DBU promoted alcoholysis of PC in MeOH/EtOH mixtures. T: 373 K; PC: ~ 0.5 g; $V_{\text{MeOH}} + V_{\text{EtOH}}$: ~ 3 mL; DBU: 0.030 mL, DBU load: ~6% (m/m), ~10 mol%.

isolated (together with 4-CP) with high yield. The process was very selective: monoethylated (256 m/z) or diethylated (284 m/z) derivatives of BPA were detected only in trace amounts. The ethanolysis reaction was slower than methanolysis (compare entry 1 and 6 in Table 8). In methanol the conversion of the polymer into BPA and DMC was complete in little more than half an hour (Entry 1, Table 8). In ethanol, under comparable conditions (Entry 6, Table 8), the full depolymerization of PC (disappearance of the pellets of polymer) required about 1 h, while the complete conversion of oligomers such as **1b** and **2b** into more BPA and DEC required a longer reaction time (3.25 h). Both **1b** and **2b** were detected in the reaction mixture by GCMS (Fig. S21 and S22). Moreover, the IR spectrum of the reaction solution registered soon after the disappearance of the pellets of polymer showed, besides the absorptions of DEC at 1748 and 1730 cm^{-1} , a band at 1763 cm^{-1} assigned to **1b** and **2b**. The latter absorption disappeared after an overall reaction time of 3.25 h, because of progressive conversion of **1b** and **2b** into BPA and DEC (Fig. 7 and Scheme 3). Therefore, in ethanol, the cleavage of the diaryl-carbonate moieties as well as the fission of the aryl alkyl carbonate groups are less easy processes than in methanol. These conclusions agree with the distribution of carbonate products observed (DMC > methyl ethyl carbonate (EMC) >> DEC) when PC was reacted in an equimolar mixture of methanol and ethanol (entry 2, Table 8).

Because of the synthetic importance that mixed carbonates have as potential precursors of unsymmetrical ethers ROR', which can be obtained from ROC(O)OR' compounds by decarboxylation,⁷² we have also focused on the depolymerization of PC in MeOH/EtOH mixtures as a route to the direct synthesis of methyl ethyl carbonate. By suitably varying the MeOH/EtOH ratio, MEC was obtained in significant yield (60 %; Table 8 and Fig. 8). This result is of interest as mixed carbonates are prepared from phosgene through a multistep procedure.

Conclusions

For the first time the alcoholysis of poly-(bisphenol A carbonate) has been investigated in the presence of an organocatalyst, such as DBU. The amidine base is an active catalyst of PC alcoholysis (eqn (1)) and, in the absence of any auxiliary solvent, promotes selectively the quantitative conversion of poly-(bisphenol A carbonate) to BPA and the relevant organic carbonate under not severe conditions (295 K - 373 K).

Using methanol as the reference alcohol, the influence of temperature, MeOH/PC ratio, DBU load and concentration on conversion time and products yield has been investigated. At 373 K, using a MeOH/PC ratio around 4.6 (m/m) and a moderate load and concentration of DBU (~10 mol% and ~10 $\text{mg}_{\text{DBU}}/\text{mL}_{\text{MeOH}}$, respectively), the selective and quantitative conversion of the polymer into BPA and DMC was achieved in about 0.5 h. Other organocatalysts, such as DABCO and DMAP, were less active than DBU. Under the working conditions, DABCO decomposed to a significant extent by reacting with DMC and converting into 1-methyl-1,4-diazabicyclo[2.2.2]octan-1-ium cation (**3**).

The study has been extended to ethanol and EtOH/MeOH mixtures. The ethanolysis reaction afforded BPA and DEC selectively and quantitatively, but proceeded more slowly than methanolysis. In MeOH/EtOH solutions BPA and a mixture of carbonates (DMC, DEC, MEC) were obtained: carbonates yield and conversion times depended on the used MeOH/EtOH molar ratio. By this way, a mixed carbonate such as ethyl methyl carbonate (MEC) was synthesized in one step with satisfactory yields (60%).

The depolymerization process does not require complex equipments, is simple from the operational point of view, does not make use of auxiliary solvents as the alcohol is used as reactant and reaction medium, is characterized by high productivity and selectivity. The catalyst can be reused *in situ* by adding fresh polymer at the end of each run and can be also recovered from the reaction mixture as adduct with BPA. Also the adduct is an effective catalyst of the alcoholysis reaction, albeit slightly less active than fresh DBU, and has been recycled several times without showing either evidence of decomposition or significant loss of activity and selectivity. All the above features are important advantages of the described process, and make it an attractive route to chemical recycling and valorization of the waste polymer.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was financially supported from Università degli Studi "Aldo Moro" di Bari (Fondi di Ateneo).

Notes and references

† Indicating with $n_{4\text{-CP}}^{\circ}$ the moles 4-cumylphenol (4-CP) incorporated in the mass w of PC feed, eqn (4) can be derived by solving the system of equations (4') and (4''),

$$n_{4\text{-CP}}^{\circ}/n_{\text{BPA}}^{\circ} = 0.035 \quad (4')$$

$$w = X_{\text{UR}} \times \text{MM}_{\text{UR}} + Y \times \text{MM}_{\text{bis(4-cumylphenyl) carbonate}} = n_{\text{BPA}}^{\circ} \times \text{MM}_{\text{UR}} + \frac{1}{2} n_{4\text{-CP}}^{\circ} \times \text{MM}_{\text{bis(4-cumylphenyl) carbonate}} \quad (4'')$$

where eqn (4'') is the mass balance stating that the mass w of PC feed consists formally of X moles of repeating units UR ($X = n_{\text{BPA}}^{\circ}$) and Y mol of bis(4-cumylphenyl) carbonate ($Y = \frac{1}{2} n_{4\text{-CP}}^{\circ}$), see also Scheme 2.

As $n_{4\text{-CP}}^{\circ} = 0.035 \times n_{\text{BPA}}^{\circ}$, then

$$w = n_{\text{BPA}}^{\circ} \times \text{MM}_{\text{UR}} + \frac{1}{2} (0.035 \times n_{\text{BPA}}^{\circ}) \times \text{MM}_{\text{bis(4-cumylphenyl) carbonate}}$$

from which eqn (4) can be obtained.

Knowing the value of n_{BPA}° , eqn (4), the moles of CO₃ groups (n_{CO_3}) contained in the mass w of PC feed (and, therefore, susceptible to take part into the alcoholysis reaction) can be calculated as follows:

$$n_{\text{CO}_3} (\text{mol}_{\text{CO}_3}) = X + Y = n_{\text{BPA}}^{\circ} + 0.5 \times n_{4\text{-CP}}^{\circ} = n_{\text{BPA}}^{\circ} + 0.5 \times 0.035 \times n_{\text{BPA}}^{\circ} \quad (5)$$

$$\ddagger \text{ DBU load (\%, m/m)} = (\text{m}_{\text{DBU}}/\text{m}_{\text{PC}}) \times 100;$$

$$\text{DBU load (mol\%)} = (\text{mol}_{\text{DBU}}/\text{mol}_{\text{CO}_3}) \times 100.$$

¶ Under comparable conditions NaOH behaved as a less effective catalyst than DBU. For instance, at 373 K, the depolymerization of 0.496 g of PC in neat MeOH (3 mL) in the presence of NaOH as catalyst (10.2 mg, 0.26 mmol; NaOH load: 13 mol%) was quantitative within 1 h. DMC and BPA yields were found equal to 99% and 96%, respectively.

§ For instance, in the FTIR spectra of DMC (liquid film) and methyl phenyl carbonate (liquid film), the stretching $\nu_{\text{C=O}}$ is observed, respectively, at 1758 and 1766 cm⁻¹. By comparison, the $\nu_{\text{C=O}}$ stretching of diphenyl carbonate is found at higher wavenumbers: 1776 cm⁻¹ (KBr disk) or at 1774 and 1762 cm⁻¹ (nujol mull).⁶⁸

Analogously, in the IR spectrum of solid PC (Fig. S1) the $\nu_{\text{C=O}}$ stretching absorbs at 1770 cm⁻¹ (1778 cm⁻¹, in THF solution⁴³).

** MS of 4: 354 (M⁺), 339 (M⁺-Me), 325, 311, 281, 268, 253, 239, 225, 213, 197, 165, 141, 127 (DABCO-Me⁺), 126 (M⁺-BPA), 113 (DABCO-H⁺; base peak), 98, 84, 70, 56, 42 m/z.

†† As a comparison, an analogous band is also present in the IR spectrum of DBU·HCl (1643 cm⁻¹) and (DBUH)BPh₄ (1645 cm⁻¹).

‡‡ For instance, compare the C_{ipso} resonance of PhO⁻ anion (168.07 ppm) with the corresponding resonance of PhOH (156.99 ppm), as calculated by means of the program ACD/C+H NMR Predictors and DB (www.acdlabs.com).

§§ Analogous remarks can account for the lower catalytic activity exhibited by the DBU-BPA adduct relative to fresh DBU (Table 7).

- 1 *Handbook of Plastic Recycling*, ed. F. La Mantia, Rapra Technology, Shrewsbury, 2002.
- 2 E. Feghali and T. Cantat, *ChemSusChem*, 2015, **8**, 980-984.
- 3 I.A. Ignatyev, W. Thielemans and B.V. Beke, *ChemSusChem*, 2014, **7**, 1579-1593.
- 4 *Material Recycling - Trends and Perspectives*, ed. D. S. Achilias, InTech, Rijeka, Croatia 2012.
- 5 HIS Markit, Newsroom, <http://press.ihs.com/press-release/commodities-pricing-cost/after-major-downturn-global-demand-polycarbonate-growing-agai>, (February 2012).
- 6 E.V. Antonakou and D.S. Achilias, *Waste Biomass Valor.*, 2013, **4**, 9-21 and references therein.
- 7 Mordor Intelligence, http://www.mordorintelligence.com/industry-reports/pc-polycarbonate-market?gclid=CKmv1NeW684CFasp0wod_r0F7w, (August 2016).
- 8 D.S. Achilias, E.V. Antonakou, E. Koutsokosta and A.A. Lappas, *J. Appl. Polym. Sci.*, 2009, **114**, 212-221.
- 9 L. Méndez-Liñán, F. J. López-Garzón, M. Domingo-García and M. Pérez-Mendoza, *Energy Fuels*, 2010, **24**, 3394-3400.

- 10 S.-J. Chiu, S.-H. Chen and C.-T. Tsai, *Waste Management*, 2006, **26**, 252-259.
- 11 L.-C. Hu, A. Oku and E. Yamada, *Polymer*, 1998, **39**, 3841-3845.
- 12 H. Jie, H. Ke, Z. Qing, C. Lei, W. Yongqiang and Z. Zibin, *Polym. Degrad. Stabil.*, 2006, **91**, 2307-2314.
- 13 F. Liu, Z. Li, S. Yu, X. Cui and X. Ge, *J. Hazard. Mater.*, 2010, **174**, 872-875.
- 14 F. Liu, L. Li, S. Yu, Z. Li and X. Ge, *J. Hazard. Mater.*, 2011, **189**, 249-254.
- 15 R. Piñero, J. García and M. J. Cocero, *Green Chem.*, 2005, **7**, 380-387.
- 16 D. Kim, B. Kim, Y. Cho, M. Han and B.-S. Kim, *Ind. Eng. Chem. Res.*, 2009, **48**, 6591-6599.
- 17 L. Rosi, M. Bartoli, A. Undria, M. Frediani and P. Frediani, *J. Mol. Catal. A: Chemical*, 2015, **408**, 278-286.
- 18 A. Oku, S. Tanaka and S. Hata, *Polymer*, 2000, **41**, 6749-6753.
- 19 C.-H. Lin, H.-Y. Lin, W.-Z. Liao and S.A. Dai, *Green Chem.*, 2007, **9**, 38-43.
- 20 M.M.A. Nikje, *Polimery*, 2011, **56**, 381-384.
- 21 D. Kim, B. Kim, Y. Cho, M. Han and B.-S. Kim, *Ind. Eng. Chem. Res.*, 2009, **48**, 685-691.
- 22 S. Hata, H. Goto, E. Yamada and A. Oku, *Polymer*, 2002, **43**, 2109-2116.
- 23 S. Hata, H. Goto, S. Tanaka and A. Oku, *J. Appl. Polym. Sci.*, 2003, **90**, 2959-2968.
- 24 R. Arai, K. Zenda, K. Hatakeyama, K. Yui and T. Funazukuri, *Chem. Eng. Sci.*, 2010, **65**, 36-41.
- 25 Z. Pan, I.-M. Chou and R.C. Burrus, *Green Chem.*, 2009, **11**, 1105-1107.
- 26 M. Watanabe, Y. Matsuo, T. Matsushita, H. Inomata, T. Miyake and K. Hironaka, *Polym. Degrad. Stabil.*, 2009, **94**, 2157-2162.
- 27 Y. Huang, S. Liu and Z. Pan, *Polym. Degrad. Stabil.*, 2011, **96**, 1405-1410.
- 28 Z. Pan, Z. Hu, Y. Shi, Y. Shen, J. Wang and I.-M. Chou, *RSC Adv.*, 2014, **4**, 19992-19998.
- 29 F.-S. Liu, Z. Li, S.-T. Yu, X. Cui, C.-X. Xie and X.-P. Ge, *J. Polym. Environ.*, 2009, **17**, 208-211.
- 30 G. Grause, N. Tsukada, W.J. Hall, T. Kameda, P.T. Williams and T. Yoshioka, *Polym. J.*, 2010, **42**, 438-442.
- 31 G. Grause, K. Sugawara, T. Mizoguchi and T. Yoshioka, *Polym. Degrad. Stabil.*, 2009, **94**, 1119-1124.
- 32 H. Tagaya, K. Katoh, J. Kadokawa and K. Chiba, *Polym. Degrad. Stabil.*, 1999, **64**, 289-292.
- 33 T. Yoshioka, K. Sugawara, T. Mizoguchi and A. Okuwaki, *Chem. Lett.*, 2005, **34**, 282-283.
- 34 K. Hatakeyama, T. Kojima and T. Funakuzuri, *J. Mater. Cycles Waste Manag.*, 2014, **16**, 124-130.
- 35 A. Ikeda, K. Katoh and H. Tagaya, *J. Mat. Sci.*, 2008, **43**, 2437-2441.
- 36 G. Grause, R. Karrbrant, T. Kameda and T. Yoshioka, *Ind. Eng. Chem. Res.*, 2014, **53**, 4215-4223.
- 37 M. Taguchi, Y. Ishikawa, S. Kataoka, T. Naka and T. Funazukuri, *Catal. Commun.*, 2016, **84**, 93-97.
- 38 G.P. Tsintzou and D.S. Achilias, *Waste Biomass Valor.*, 2013, **4**, 3-7.
- 39 X. Song, F. Liu, L. Li, X. Yang, S. Yu and X. Ge, *J. Hazard. Mater.*, 2013, **244-245**, 204-208.
- 40 L. Li, F. Liu, Z. Li, X. Song, S. Yu and S. Liu, *FIBER POLYM*, 2013, **14**, 65-368.
- 41 N. Deirram and A.R. Rahmat, *APCBEE Procedia*, 2012, **3**, 172-176.
- 42 M.M.A. Nikje and M. Askarzadeh, *Polymery*, 2013, **58**, 292-294.
- 43 E. Quaranta, *Appl. Catal. B: Environmental*, 2017, **206**, 233-241.
- 44 K. Troev, R. Tsevi and I. Gitsov, *Polymer*, 2001, **42**, 39-42.

Journal Name

- 45 S.-J. Chiu, C.T. Tsai and Y.-K. Chang, *e-Polymers*, 2008, n.132; doi.org/10.1515/epoly.2008.8.1.1516.
- 46 Z.-Y. Pan, X. Zou, H.-M. Jin, H.-M. Li, H. Lin, H.-Y. Zhou and C.-M. Lin, *Journal of Chemical Engineering of Chinese Universities*, 2008, **22**, 597-603.
- 47 Y. Fang, H. Jin, Z. Pan, X. Zou and C. Lin, *Huagong Xuebao*, 2009, **60**, 372-377.
- 48 P.W. Bell, V.I. Fernandez, V.R. G. Bhotla, T. Gunale, A. Stanislaus and D. Jayanna, US 9428627, 2016.
- 49 Z.-Y. Pan, Z. Bao and Y.X. Chen, *Chin.. Chem Lett.*, 2006, **17**, 545-548.
- 50 M. Carafa and E. Quaranta, *Mini-Rev. Org. Chem.*, 2009, **6**, 168-183.
- 51 E. Quaranta and M. Aresta, *The Chemistry of N-CO₂ bonds: Synthesis of Carbamic Acids and their Derivatives, Isocyanates, Ureas in Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH Verlag GmbH & Co.KGaA, Weinheim, 2010, 121-167.
- 52 M. Aresta and E. Quaranta, *Chemtech*, 1997, **27(3)**, 32-40.
- 53 M. Carafa, V. Mele and E. Quaranta, *Green Chem.*, 2012, **14**, 217-225.
- 54 D. Ballivet-Tkatchenko and A. Dibenedetto, *Synthesis of Linear and Cyclic Carbonates in Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH Verlag GmbH & Co.KGaA, Weinheim, 2010, pp.169-212.
- 55 D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shelada and P.J. Dunn, *Green Chem.*, 2016, **18**, 288-296.
- 56 E. Quaranta, M. Carafa and F. Trani, *Appl. Catal. B: Environ.*, 2009, **91**, 380-388.
- 57 M. Carafa, M. Distaso, V. Mele, F. Trani and E. Quaranta, *Tetrahedron Lett.*, 2008, **49**, 3691-3696.
- 58 M. Carafa, F. Iannone, V. Mele and E. Quaranta, *Green Chem.*, 2012, **14**, 3377-3385.
- 59 M. Carafa, E. Mesto and E. Quaranta, *Eur. J. Org. Chem.*, 2011, 2458-2465.
- 60 E. Quaranta, A. Angelini, M. Carafa, A. Dibenedetto and V. Mele, *ACS Catal.*, 2014, **4**, 195-202.
- 61 D.J. Brunelle, P.M. Smigelski Jr. and E.P. Boden, *ACS Symposium Series*, 2005, Vol. **898**, Chapter 2 (Advances in Polycarbonates), 8-21.
- 62 E.R. Perez, R.H.A. Santos, M.T.P. Gambardella, L.G.M. de Macedo, U.P. Rodrigues-Filho, J.C. Launay and D.W. Franco, *J. Org. Chem.*, 2004, **69**, 8005-8011.
- 63 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford (1986).
- 64 F. Aricò and P. Tundo, *Russian Chem. Rev.*, 2010, **79**, 479-489.
- 65 W.C. Shieh, S. Dell and O. Repič, *Org. Lett.*, 2001, **3**, 4279-4281.
- 66 H. Schnell and H. Krimm, *Angew. Chem. Int. Edit.*, 1963, **2**, 373-379.
- 67 S.E. Hunter and P.E. Sauvage, *J. Org. Chem.*, 2004, **69**, 4724-4731.
- 68 SDBS Information. http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi
- 69 N. Maräs, S. Polanc and M. Kõcevar, *Org. Biomol. Chem.*, 2012, **10**, 1300-1310.
- 70 P. H. Vendramini, B. R. Vilachã Ferreira and M. N. Eberlin, Probing the Mechanism of N-Methylation of Indole with Dimethylcarbonate by ESI-MS, 5^o Congresso Brasileiro de Espectrometria de Massas, 2013; <http://www.brmas.com.br/congresso/resumos/3P1929.pdf>
- 71 K. Shuklaa and V.C. Srivastava, *RSC Adv.*, 2016, **6**, 32624-32645
- 72 P. Tundo, F. Aricò, A. E. Rosamilia and S. Memoli, *Green Chem.*, 2008, **10**, 1182-1189.