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Chemical Recycling of Poly-(Bisphenol A Carbonate) by Diaminolysis: a New Carbon-Saving Synthetic Entry into Non-Isocyanate Polyureas (NIPUreas)

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ABSTRACT

The present study describes an unprecedented approach to valorize potentially hazardous poly-(bisphenol A carbonate) (PC) wastes. In THF, under non-severe conditions (120 °C), the reaction of PC with long-chain diamines H_2NRNH_2 (2 equivalents) provided a tool to regenerate the monomer bisphenol A (BPA; 83-95%, isolated) and repurpose waste PC into [-NHRNHCO-]$_n$ polyureas (PUs; 78-99%, isolated) through a non-isocyanate route. Basic diamines (1,6-diaminohexane, 4,7,10-trioxa-1,13-tridecanediamine, *meta*-xylylenediamine, *para*-xylylenediamine) reacted with PC without any auxiliary catalyst; less reactive aromatic diamines (4,4'-diaminodiphenylmethane, 2,4-diaminotoluene) required the assistance of a base catalyst (1,8-diazabicyclo[5.4.0]undec-7-ene, NaOH). The formation of [-NHRNHCO-]$_n$ goes through a carbamation step affording BPA and carbamate intermediates H[-OArOC(O)NHRNHC(O)-]$_n$OArOH (Ar = 4,4'-$C_6H_4C(Me)_2C_6H_4$-) that, in a subsequent step, convert into [-NHRNHCO-]$_n$ and more BPA. All the PUs were characterized in the solid state by CP/MAS ^{13}C-NMR (δ(C=O) = 152-161 ppm) and IR spectroscopy. The positions of ν(N-H) and ν(C=O) absorptions are typical of "hydrogen-bonded ordered" bands supporting the presence of H-bonded groups in network structures characterized by some degree of order or regularity. DSC and TGA analyses showed that the PUs are thermally stable ($T_{d,5\%}$: 212-270 °C) and suitable for being processed since their degradation begins at temperatures about 100 °C higher than their T_g or T_m.

Keywords: BPA; polycarbonate; polyureas; waste plastic valorization; circular economy

ABBREVIATIONS:
ATR: Attenuated Total Reflectance; BPA: 2,2-bis(4-hydroxyphenyl)propane, bisphenol A; CAGR: Compound Annual Growth Rate; CP/MAS: Cross Polarization Magic-Angle Spinning; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; DSC: Differential Scanning Calorimetry; HMDA: 1,6-diaminohexane; MDA: 4,4'-diaminodiphenylmethane; NIPUreas: Non-Isocyanate PolyUreas; PC: Poly-(bisphenol A carbonate); PU: polyurea; TDA: 2,4-diaminotoluene; TGA: Thermogravimetric Analysis; TMS: tetramethylsilane; TOSS: Total Sideband Suppression; TOTDA: 4,7,10-trioxa-1,13-tridecanediamine; UR(PC): repeating unit of PC; *m*-XYLDA: *meta*-xylylenediamine; *p*-XYLDA: *para*-xylylenediamine.

1. Introduction

Polymeric materials have experienced a widespread rapid diffusion in our daily life. However, as a consequence of linear way of consuming plastics, these materials have been accumulating in the environment and have generated health, environmental and social concerns that make necessary a change of strategy, such as shifting to a circular and environmentally sustainable plastic economy based on the recycling of these materials at the end of their life-cycle [La Mantia, 2002; Ragaert et al., 2017; Fortman et al., 2018]. In the last few years chemical recycling of plastics has been gaining great attention as a methodological approach to reduce the environmental and social impact of this type of wastes, providing thus a potential tool to generate a sustainable supply chain for a variety of polymeric materials. This approach, that implies the chemical conversion of the waste polymer into added-value chemicals, is not only a captivating alternative to landfill or energy recovery, but also a smart response to the current worldwide need of saving carbon and energy and protecting fossil resources from depletion [Datta and Kopczynska, 2016; Rahimi and Garcia, 2017; Hong and Chen, 2017; Jehanno et al., 2019; Shao et al., 2020].

Poly-(bisphenol A carbonate) (PC), currently accessible through phosgeneless synthetic routes [Kim, 2020], is one of the most widely used thermoplastics. PC global market is steeply expanding and is projected to reach approximately 5.1 million tons by the end of 2023, increasing at a CAGR of around 3% per year in the period 2017-2023 [Asscoated Press News, 2018]. The fast increase of manufacture and utilization of PC raises the problem of the fate of the wastes of this material. The polymer is a potential reservoir of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), a known xenoestrogen and endocrine disruptor, that is potentially harmful to both wildlife, including marine organisms, and humans [Tucker et al., 2018]. Prevention of BPA leaching into the environment through uncontrolled hydrolysis or biodegradation of the waste polymer is matter that deserves due attention as BPA release into the environment may have adverse repercussions on many living organism and human health.

These concerns call for the development of environmentally friendly and cost-efficient post-consumer PC treatments. Chemical recycling of waste PC can provide a convenient answer to this issue, as it opens a way to the valorization of the waste polymer [Antonakou and Achilias, 2013; Datta and Kopczynska 2016; Hong and Chen, 2017; Kim, 2020]. In this ambit different approaches can be pursued, such as pyrolysis [Wang et al., 2020], reduction (hydrogenation, hydrosilylation) [Monsigny et al., 2018; Westhues et al., 2018; Alberti et al., 2020a], or also other options based on the chemical fission of carbonate bond by hydrolysis [Taguchi et al., 2016; Quaranta, 2017; Liu et al., 2018], alcoholysis [Quaranta et al., 2017; Liu et al., 2019; Alberti et al., 2020b], phenolysis [Alberti et al., 2019], glycolysis [Iannone et al., 2017; Quaranta et al., 2018; Do et al., 2018; Jehanno et al., 2020], aminolysis [Hata et al., 2002; Singh et. al., 2015; Iannone et al., 2017; Wu et al., 2018; Demarteau et al., 2020]. The latter methods allow to regenerate the monomer, bisphenol A, that can be reused to produce new virgin PC, or polymeric materials different from PC (for instance, poly(aryl ether sulfone)s) [Jones et al., 2016], or also converted into other products such as, for example, jet fuel range high-density polycycloalkanes [Tang et al., 2019]. However, these approaches can also cogenerate high added value chemicals besides BPA, such as carbonic acid diesters or organic carbamates and ureas if the polymer is reacted respectively with alcohols or amines. In the latter cases waste PC can be used as a carbonylating agent succedaneous of harmful phosgene [Hata et al., 2003; Carafa and Quaranta, 2009].

Herein we have focused on the aminolysis reaction. Relative to other PC depolymerization methods, the reaction of PC with amine substrates has received rather poor attention in the past and, only occasionally, has been explored as a way to recycle the polymer (PC) chemically [Hata et al., 2002; Singh et. al., 2015; Iannone et al., 2017; Wu et al., 2018; Demarteau et al., 2020]. Depending on the experimental conditions and the nature of amine (primary or secondary), the depolymerization of PC with mono-amines can afford, besides BPA, carbamates or acyclic mono-ureas RR'NC(O)NRR' (R = H, R' = alkyl, aryl; R = R' = alkyl) in variable yields [Hata et al., 2002; Singh et. al., 2015; Iannone et al., 2017; Demarteau et al., 2020]. The reaction of the polycarbonate

with short-chain diamines, such as *N,N'*-dimethyl-1,2-diaminoethane or *N,N'*-dimethyl-1,3-diaminopropane, 1,2-diaminopropane, 1,3-diaminopropane, has been exploited for the synthesis of the relevant cyclic ureas [Hata et al., 2002; Iannone et al., 2017]. Very recently, PC was reacted with aliphatic primary diamines to give hydroxyl-*N,N'*-diphenylene-isopropylidenyl biscarbamate prepolymers that, in a subsequent Sn-catalyzed step, were chain-extended with commercially available diisocyanates to produce a variety of polyurethanes [Wu et al., 2018].

Relative to the above studies [Hata et al., 2002; Singh et. al., 2015; Iannone et al., 2017; Wu et al., 2018; Demarteau et al., 2020], in this work we have followed an unprecedented approach to valorize PC wastes as the reaction of PC with a few long-chain diamines has been explored as a way to regenerate the monomer and, for the first time in the literature, repurpose waste PC into virgin polyureas (PUs) straightforwardly, in a one-pot process (Fig. 1). In virtue of their special properties (resistance to hydrolysis, oxidation and abrasion; excellent mechanical and anti-corrosion properties; thermal stability at high temperatures; biocompatibility) polyureas have been finding wide application in several fields (coatings, greases, membranes, microcapsules, biomedical devices) [Pires et al., 2000]. Quite recently, these compounds have been successfully used as starting materials for the phosgeneless synthesis of R'O(O)CNHRNHC(O)OR' dicarbamates [Shang et al., 2012], widely used in industry as precursors of polyurethanes.

PUs are traditionally prepared by polyaddition of diamines and diisocyanates [Pires et al., 2000]. The toxicity of isocyanates has urged both academia and industry to explore more environmentally friendly isocyanate-free methods of synthesis of polyureas (Non-IsocyanatePolyUreas (NIPUreas)): for instance, the reaction of diamines with carbonyl sources such as carbon dioxide [Rockicki, 1988; Shang et al., 2012; Wu et al., 2012; Ying et. al. 2015; Wang et al., 2016], urea [Dennis et al., 2018], diphenyl carbonate [Pan et al., 2015], or also dialkyl dicarbamates R'O(O)CNHRNHC(O)OR'[Ma et al., 2018], that, recently, have been converted into NIPUreas by metathesis polymerization in the presence of a base catalyst [Kébir et al., 2017]. Herein, we report on a new route to polyureas that, as an outstanding peculiarity, conjugates the

feature of avoiding any use of hazardous isocyanates with the advantages of recycling a potentially hazardous waste polymer (PC) and saving carbon (Fig. 1).

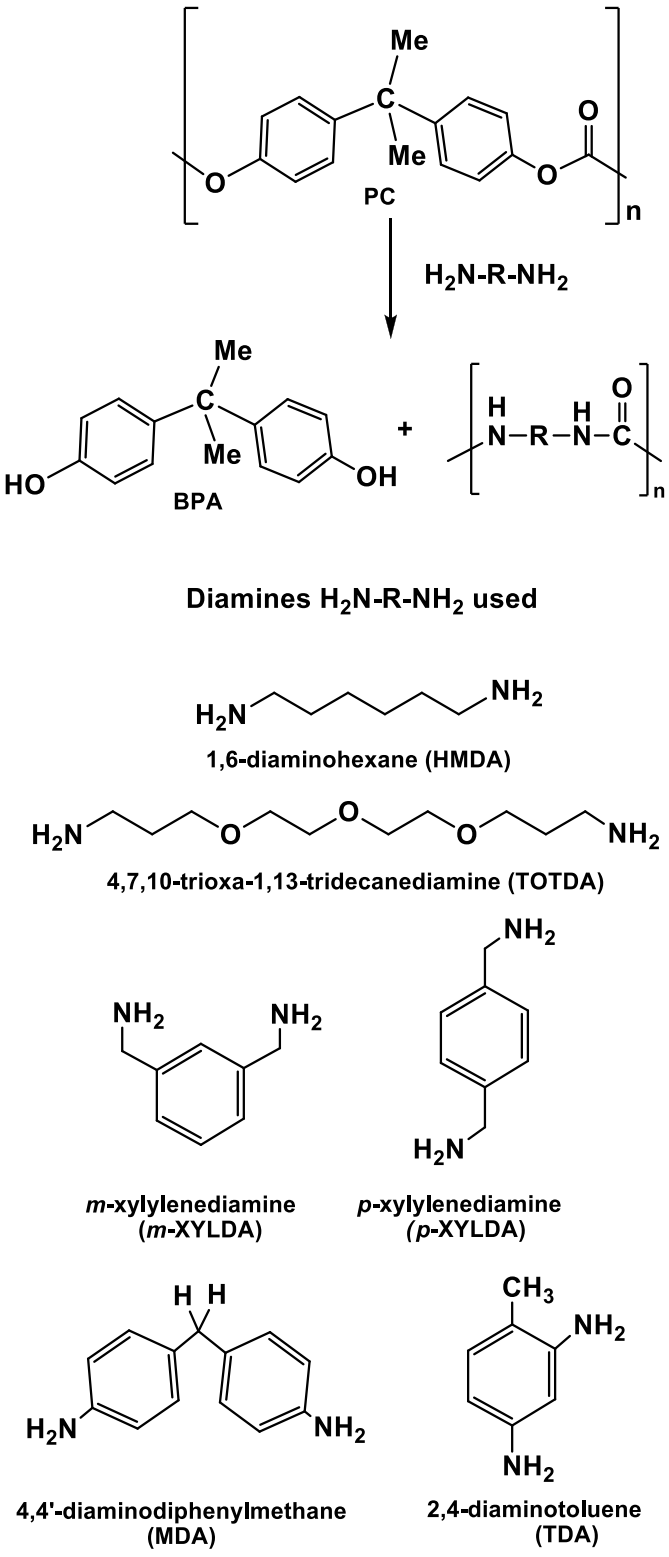


Fig. 1. Repurposing of waste PC into polyureas.

2. Experimental

2.1. General methods and materials

Vacuum line techniques were used for manipulations carried out under inert atmosphere (N_2). THF and diethyl ether were dried according to standard procedures (P_2O_5; Na/benzophenone) [Perrin et al., 1986]. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the diamines (Fig. 1) were from Aldrich and were used as received except HMDA that was purified by sublimation before use. Both DBU and the basic diamines HMDA, TOTDA, *m*-XYLDA, *p*-XYLDA were manipulated under N_2 to prevent any contamination from atmospheric CO_2 or moisture. PC pellets (SABIC; 3 mm length × 2 mm diameter) were used as a model of waste polycarbonate. The characterization of the polymer was reported elsewhere [Quaranta et al., 2018]. The moles of BPA ($n°_{BPA}$) incorporated in *w* grams of feed polycarbonate were assumed to be equal to the moles of repeating unit of PC (UR(PC)), $n_{UR(PC)}$, and were calculated according to Eq. (1), where $MM_{UR(PC)}$ is the molar mass of the UR(PC) (254.29 g/mol; Fig. 1).

$$n°_{BPA} = n_{UR(PC)} = w/MM_{UR(PC)} \quad (1)$$

GC analyses were performed with a THERMO Scientific TRACE 1310 gas-chromatograph (GC column: Heliflex AT-5, 30 m × 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. ^{13}C NMR cross polarization magic angle scanning (CP/MAS) measurements were performed at 151 MHz on a Bruker AVANCE 600 apparatus equipped with a MAS II Pneumatic Unit, using TOSS technique. Solid sample was packed in a 4 mm zirconia rotor with a Kel-F cap and spinning at 11 kHz during the analysis (delay time = 4 s). CP/MAS ^{13}C chemical shifts of solid samples are referenced to the resonance of adamantane at 29.5 ppm. ^{1}H and ^{13}C NMR chemical shifts of samples in solution are in δ (ppm) versus TMS. The

thermal properties of the polyureas were investigated by DSC (Q200 TA Instruments) and TGA (Pyris 1-Perkin Elmer) under a nitrogen flow of 50 mL/min at the heating rate of 10 °C/min. The TGA experiments were performed from 40 °C to 800 °C. In the DSC experiments the samples were heated, cooled and heated again from 0 °C to a maximum temperature determined by the thermal stability of each sample, as evaluated by TGA measurements. The first DSC heating run was used to remove any thermal effect that may hide transitions such as, for instance, glass transitions or melting. Glass temperature was determined at the inflection of the step in the baseline, whereas the melting temperature at the maximum of the endothermic peak. Both DSC and TGA measurements were carried out in duplicate obtaining reproducible results.

2.2. Calculation of BPA and polyurea (PU) yield

BPA yield was calculated through Eq. (2), where n_{BPA} are the moles of biphenol A isolated from the reaction mixture.

$$\text{BPA yield (\%)} = (n_{BPA}/n°_{BPA})\times 100 \quad (2)$$

PU yield was calculated according to Eq. (3), where w_{PU} is the mass (g) of PU isolated and MM_{PU} is the molar mass of the PU repeating unit.

$$\text{PU yield (\%)} = 100\times(w_{PU}\times MM_{UR(PC)})/(w\times MM_{PU}) \quad (3)$$

2.3. Determination of PC conversion

PC conversion in aminolysis experiments was determined spectrophotometrically by measuring in the FTIR spectrum of the reaction mixture the intensity of the residual absorption at 1778 cm^{-1} due to ν(C=O) stretching in -OArO*C(O)*OArO- (Ar = 4,4'-$C_6H_4CMe_2C_6H_4$-) moieties of the starting polymer or its oligomers/fragments not completely depolymerized. The intensity of this signal was compared with the intensity of the absorption displayed, at the same wavenumber, by standard THF solutions of polycarbonate. PC conversion was, then, calculated through Eq. (4), wherein *w*(g) is the mass of feed PC

and w_1(g) is the overall amount of polymer/oligomers not yet depolymerized and determined spectrophotometrically by FTIR.

PC conversion (%) = $100\times(w - w_1)/w$ (4)

2.4. H_2NRNH_2 carbamation by PC diaminolysis (diamine/UR(PC) stoichiometric ratio: 0.5 mol/mol)

As an example, we report the procedure followed with HMDA. The reaction was carried out in a suitable glass tube (~40 mL) equipped with a Sovirel screw cap and a Torion stopcock. The reactor, once charged with the reactants (PC, usually ~4 $mmol_{UR(PC)}$; HMDA, 1-1.14 equivalents; solvent (THF), usually 24 mL), was sealed and dipped into an electrically heated silicon oil bath and the reaction mixture was stirred at the working temperature until complete PC depolymerization, that was ascertained by monitoring the disappearance of the polycarbonate absorption at 1778 cm^{-1} in the FTIR spectrum of the reaction mixture (Figs. S1a-S1c). Once PC conversion was complete, the reaction solution was evaporated in vacuum and the residue was washed several times with diethyl ether. The white solid insoluble in ether, once dried under vacuum, was analyzed by spectroscopic methods (NMR and FTIR; Fig. S2a-S2c).

Depending on the reaction temperature (at 100 °C, for instance) minor amounts of a colorless solid may separate from the reaction mixture. The FTIR spectrum of this material, once isolated by filtration, showed bands typical of ureidic groups (see 3.1 and Fig. S1d).

2.5. PC recycling by diaminolysis: BPA recovery and synthesis of PUs [-NHRNHCO-]$_n$

The diaminolysis reaction was carried out in a reactor analogous to that described above (2.4). In a typical experiment the reactor, once charged under an inert gas stream with the reactants (PC; diamine (2 equivalents); solvent (THF); catalyst (DBU or NaOH), if used), was sealed and dipped into an electrically heated silicon oil bath. The mixture was stirred at the working temperature (120 °C) for a variable time, depending on the diamine

and the catalyst, if used (see 3.2 and Table 1 and 2). The solid precipitated was isolated by filtration and identified as polyurea, while BPA was recovered from the filtrate after removing THF. For further details see Tables 1 and 2, and Appendix A (Supplementary Data).

3. Results and discussion

Fig. 1 shows the diamines H_2NRNH_2 considered in this study. We have focused on industrially relevant diamines with a suitable spacer group R such as to prevent the undesired side-formation of cyclic ureas. The diaminolysis reaction was studied in THF, a solvent that easily dissolves PC as well as the diamines used.

3.1. H_2NRNH_2 carbamation by PC diaminolysis

The diaminolysis reaction was first studied using a 0.5 mol/mol diamine/UR(PC) stoichiometric ratio (diamine: 1 equivalent). This reaction was expected to afford urethane chains like **1**, besides BPA (Fig. 2). We selected an aliphatic diamine such as HMDA as the

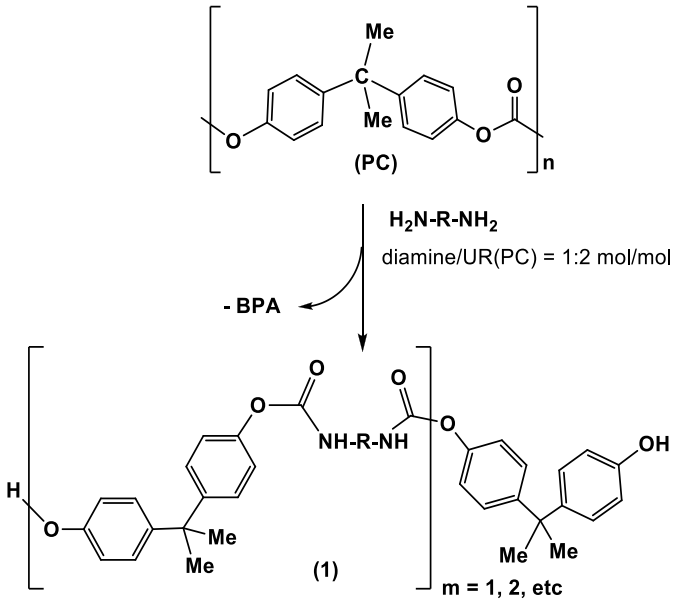


Fig. 2. PC diaminolysis (diamine/UR(PC) = 0.5 mol/mol): H_2NRNH_2 carbamation.

reference diamine. The progress of the reaction was monitored by following, in the IR spectrum of the reaction solution (Figs. S1a-c), the disappearance of the PC carbonyl absorption at 1778 cm^{-1} and the growth of the band at 1746 cm^{-1} due to ν(C=O) carbamic stretching in urethanic species like **1** (R = -$(CH_2)_6$-) [Pan et al., 2015; Quaranta, 2017]. The formation of the latter species was accompanied by that of BPA, which is responsible for the signals observed at 1614 and 1591 cm^{-1} [Quaranta, 2017].

The urethane derivatives **1** (R = -$(CH_2)_6$-) cogenerated with BPA were isolated (see 2.4) and analyzed by FTIR and NMR spectroscopy. The IR spectrum shows the intense absorption of carbamate group at 1711 cm^{-1} (Fig. S2a) [Wu et al., 2018; Mattia and Painter, 2007; Distaso and Quaranta, 2004a; Aresta et al., 1998]. The aliphatic region of the ^{1}H NMR spectrum (Fig. S2b) displays the resonances due to the methylene protons of bis-carbamated HMDA at 1.28 (br), 1.44 (br), 3.03 ppm (br) [Distaso and Quaranta, 2006]; accordingly, a broad resonance is also present at 7.68 ppm that can be assigned to the carbamic N*H* protons. The absence of any methylene C$H_2$$NH_2$ resonance around 2.6 ppm allows to exclude the presence of chains ending with free NH_2 groups, while the O*H* singlet at 9.17 ppm is consistent with the presence of urethanic chains **1** (R = -$(CH_2)_6$-) bearing terminal -OArOH (Ar = 4,4'-$C_6H_4CMe_2C_6H_4$-) groups **A** (Fig. 3), which are also responsible for the signals at 7.16 (m), 6.97 (m), 6.64 (d, $^3J_{HH}$ = 8.8 Hz) and 1.56 ppm (s); the

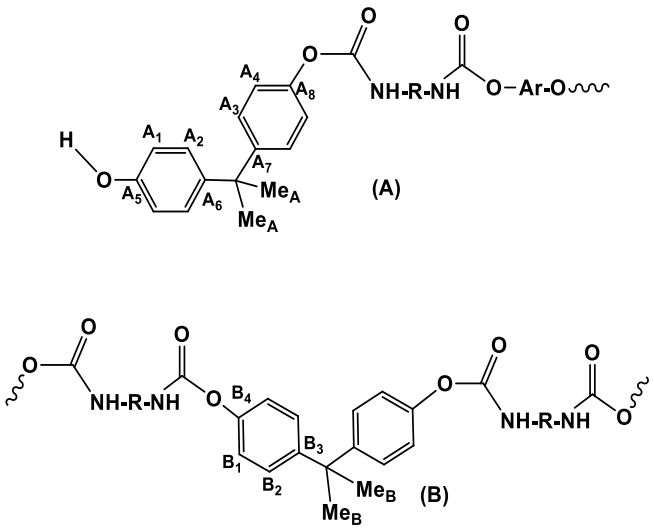


Fig. 3. Atom numbering in terminal -OArOH groups **A** and inner -OArO- groups **B**.

signals at 7.16 and 6.97 ppm are also due to inner -OArO- moieties **B** (Fig. 3), as well as the singlet at 1.61 ppm. The analysis of the integral spectrum allows to calculate the molar ratio between terminal -OArOH groups **A** and inner -OArO- groups **B**, which is ~1.5 mol/mol, as well as the number average molecular weight M_n that was found to be close to 1200 Da. The inspection of the ^{13}C-NMR spectrum (Fig. S2c) further supports the partial depolymerization of the polycarbonate with the incorporation of the diamine in the PC framework and the formation of **1** (R = -$(CH_2)_6$-).

The carbamation reaction proceeded without any auxiliary catalyst under very mild conditions (25-60 °C) with practically quantitative PC conversion (≥ 98% after 9 h; Fig. 4, curve (a) and (b)) and selectively, without any evidence of formation of ureidic derivatives. Accordingly, the IR spectrum of the reaction mixture, that kept homogeneous throughout the reaction time (no formation of precipitate), did not show, in the relevant range 1700-1620 cm^{-1}, any significant absorption which might be diagnostic of the presence of ureidic species (free or associated) in solution [Mido, 1973; Lortie et al., 2003]. Under the working conditions (Fig. 4, curve (a) and (b)), the conversion rate, while being satisfactory soon after mixing the reactants, with PC conversion higher than 80% after 1 h, slowed down a lot in the long run and the full conversion of the polycarbonate required a markedly longer time. This behavior can be obviously related to the lower and lower concentration of the reactants in the reaction mixture, but may also reflect the fact that the aminolysis of organic carbonates is usually promoted by amine itself, since a second molecule of amine can act as the catalyst of the carbamation process [Carafa and Quaranta, 2009; Um et al., 2018]. This accounts for the modest excess of diamine (max. 13 mol% relative to UR(PC)) usually used in the carbamation experiments.

At 100 °C (Fig. 4, curve (c)) the conversion of PC was faster, but, at this temperature, under the working conditions, minor amounts of a poorly soluble colorless solid separated

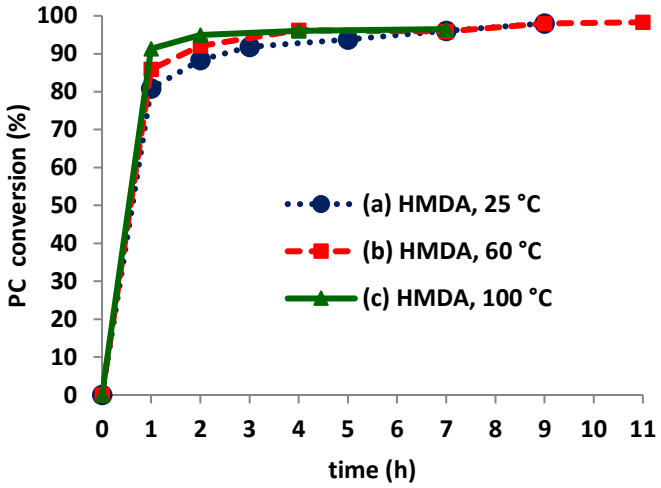


Fig. 4. HMDA carbamation by PC diaminolysis at different temperatures, in THF (24 mL). Experimental conditions: (a) UR(PC), 4.28 mmol; HMDA, 2.40 mmol; 25 °C. (b) UR(PC), 3.99 mmol; HMDA, 2.26 mmol; 60 °C. (c) UR(PC), 4.23 mmol; HMDA, 2.38 mmol; 100 °C.

with time from the reaction mixture. In the FTIR spectrum of this material (Fig. S1d) two characteristic bands at 1614 (m-s) and 1576 cm^{-1} (m-s), assignable to ureidic moieties [Mido, 1972; Aresta et al., 1998] (see also 3.2.1), can be easily recognized among the other absorptions, showing that a concurrent ureidization reaction can occur at 100 °C in addition to the carbamation process.[1] As illustrated in Fig. 5, the ureidization reaction can compete with carbamation for the functionalization of the NH_2 groups and this, in the absence of a suitable excess of diamine, can prevent the conversion of the -OC(O)O- carbonate groups from being quantitative. Accordingly, in the experiment (c) of Fig. 4 PC conversion did not exceed 97% even after prolonged heating (7 h) at the working temperature (100 °C).

The study was extended to TOTDA and *m*-XYLDA. Both the diamines reacted with PC likewise HMDA to give urethane derivatives **1** (R = $-(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3-$; *m*-$CH_2C_6H_4CH_2$-; ν(C=O): ~1746 cm^{-1}, in THF solution). At ambient temperature (25 °C),

[1] Apart from the absorptions at 1614 and 1576 cm^{-1}, the FTIR spectrum of the solid precipitated (Fig. S1d) showed strong similarities with that of **1** (R = $-(CH_2)_6-$; Fig. S2a), suggesting the precipitation, under the working conditions, of ureidic-urethanic species.

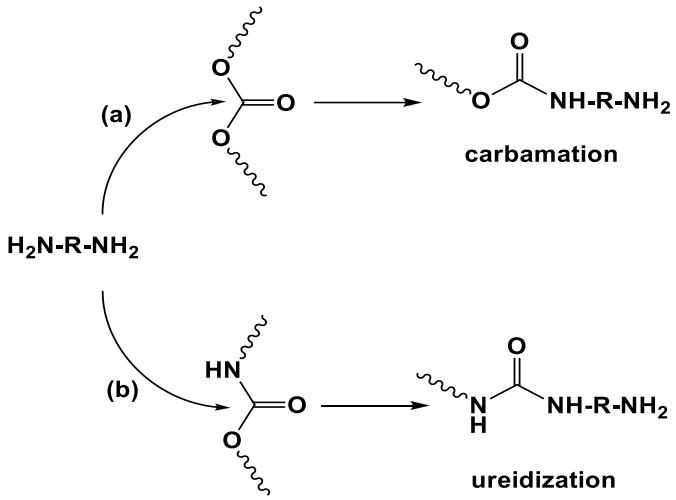


Fig. 5. PC diaminolysis: carbamation versus ureidization.

under conditions analogous to those used for HMDA, the carbamation of TOTDA and *m*-XYLDA proceeded homogenously with very high selectivity without any evidence of formation of ureidic species (no absorptions between 1700 and 1620 cm^{-1}; Fig. S3 and S4). Fig. 6 allows to compare, from the kinetic point of view, the behavior of HMDA, TOTDA and *m*-XYLDA as depolymerizing agents of the polycarbonate at ambient temperature. The kinetic curves support the following order of reactivity: TOTDA≅ HMDA > *m*-XYLDA.

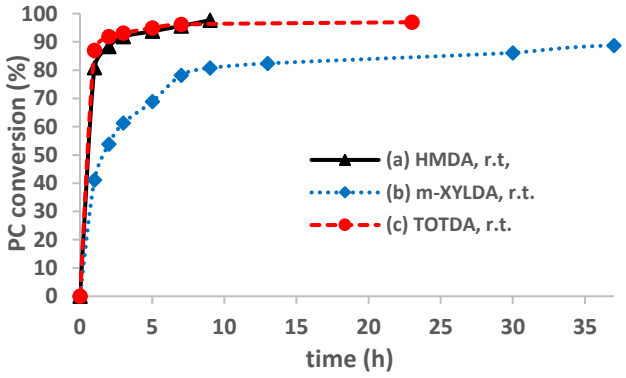


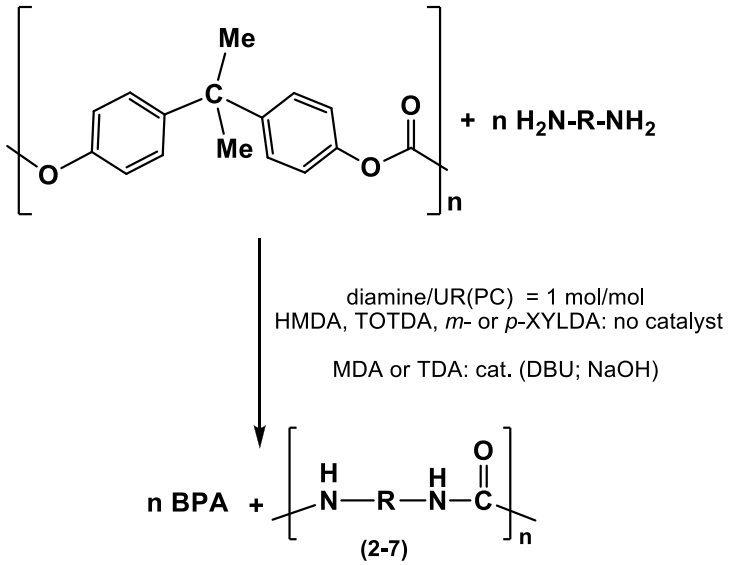
Fig. 6. Carbamation of HMDA (a), *m*-XYLDA (b) and TOTDA (c) by PC diaminolysis at room temperature (25 °C). (a) UR(PC), 4.28 mmol; HMDA, 2.40 mmol; THF, 24 mL. (b) UR(PC), 3.99 mmol; *m*-XYLDA, 2.27 mmol; THF, 24 mL. (c) UR(PC), 2.07 mmol; TOTDA, 1.14 mmol; THF, 12 mL.

In the absence of any catalyst, the aromatic diamine MDA did not react with PC under conditions analogous to those described above for the basic diamines HMDA, TOTDA and *m*-XYLDA. This behavior is not unexpected in view of the lower nucleophilicity of aromatic versus aliphatic amines and is reminiscent of the poor reactivity exhibited by MDA (as well as TDA) with diphenyl carbonate and other carbonic acid diesters in the absence of any catalyst [Aresta et al., 1995; Aresta et al., 1999; Distaso and Quaranta, 2004b].

3.2. Poly-(bisphenol A carbonate) recycling by diaminolysis: synthesis of polyureas

The above experiments suggest that relatively high temperatures can lower the selectivity of the urethanization process (Fig. 2) and promote the ureidization reaction (Fig. 5, (b)). Such a reactivity has been exploited from the synthetic standpoint with a view to providing a new synthetic entry into non-isocyanate homo-polyureas using PC as the source of the carbonyl group (Fig. 7). To this end the diamine/UR(PC) stoichiometric ratio was suitably changed and H_2NRNH_2 (2 equivalents) was reacted according to an equimolar ratio relative to the repeating unit of the polymer. Also in this case THF was selected as the solvent of the aminolysis process.

Table 1 summarizes the results obtained at 120 °C when using the basic diamines HMDA, TOTDA, *m*-XYLDA and *p*-XYLDA. Under the working conditions the conversion of the polymer into BPA and the relevant polyureas (HMDA-PU, TOTDA-PU, *m*-XYLDA-PU and *p*-XYLDA-PU, respectively) proceeded smoothly, within reasonable times that, however, may vary sensibly with the used diamine. At the working temperature HMDA-PU, *m*-XYLDA-PU and *p*-XYLDA-PU were poorly soluble in the reaction medium and separated as colorless solids. Under analogous conditions TOTDA reacted likewise HMDA, *m*-XYLDA and *p*-XYLDA, but, in the latter case, the aminolysis reaction proceeded homogeneously as the relevant polyurea (TOTDA-PU) was soluble in the reaction solvent at the working temperature (120 °C). The precipitation of



H_2N-R-NH_2	[-NH-R-NHC(O)-]$_n$		
HMDA	HMDA-PU	(**2**)	R = -$(CH_2)_6$-
TOTDA	TOTDA-PU	(**3**)	R = -$(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3$-
m-XYLDA	*m*-XYLDA-PU	(**4**)	R = *m*-$CH_2C_6H_4CH_2$-
p-XYLDA	*p*-XYLDA-PU	(**5**)	R = *p*-$CH_2C_6H_4CH_2$-
MDA	MDA-PU	(**6**)	R = 4,4'-$C_6H_4CH_2C_6H_4$-
TDA	TDA-PU	(**7**)	R = 2,4-C_6H_3Me-

Fig. 7. PC recycling by diaminolysis: synthesis of polyureas.

Table 1

PC depolymerization with the basic diamines HMDA, TOTDA, *m*-XYLDA and *p*-XYLDA (diamine/UR(PC) ≅ 1 mol/mol) at 120 °C: synthesis of homo-polyureas.

diamine (mmol)	UR(PC) (mmol)	THF (mL)	time (h)[a]	BPA (%)[b]	PU (%)[b]
HMDA (4.62)	4.05	15	2	83	HMDA-PU (96)
TOTDA (4.56)	4.00	15	2	85	TOTDA-PU (78)
m-XYLDA (4.55)	3.94	15	3.5	86	*m*-XYLDA-PU (94)
p-XYLDA (2.26)	1.93	7.5	12	83	*p*-XYLDA-PU (99)

[a] Overall reaction time. At this time the depolymerization of PC was quantitative: the IR absorption at ~1745 cm^{-1} (due to intermediate urethanic species **1**, see 3.1) was no longer visible in the FTIR spectrum of the reaction mixture.

[b] Isolated yield.

328 TOTDA-PU was observed only upon cooling the reaction mixture to room temperature.[2] In all the
329 cases BPA formed selectively without any significant formation of decomposition products (PhOH;
330 4-isopropenylphenol; 4-isopropylphenol) [Quaranta, 2017].

331 The process can be easily followed by FTIR spectroscopy (Figs. S5-S8). The
332 depolymerization of the polycarbonate goes through a carbamation step affording BPA and
333 urethane intermediates H[-OArOC(O)NHRNHC(O)-]$_n$OArOH (Ar = 4,4'-$C_6H_4C(Me)_2C_6H_4$-
334), that, in a subsequent step, convert into [-NHRNHCO-]$_n$ and more BPA. This reaction
335 sequence is well documented in Figs. S5-S8 for the ureidization of HMDA, TOTDA, *m*-
336 XYLDA an *p*-XYLDA, respectively. The intermediate formation of the urethane derivatives
337 **1** is unambiguosly supported in the FTIR spectrum of the reaction mixture by the
338 appearance of the absorption at about 1745 cm^{-1} (see 3.1); the latter absorption disappeared
339 with time because of conversion of the carbamate intermediates H[-
340 OArOC(O)NHRNHC(O)-]$_n$OArOH into the target PUs. It is worth noting that the IR
341 spectrum of the reaction solution (Figs. S5-S8) did not show any significant absorption in
342 the range 2275-2240 cm^{-1}, where isocyanate group strongly absorbs. This brings to exclude
343 that the building up of the ureidic group might imply the amination of isocyanate
344 intermediates formed *in situ* from **1**. More likely, the formation of the -NHC(O)NH-
345 moieties involves the direct attack of free NH_2 to the carbamic groups of **1**.

346 PC depolymerization by the aromatic diamine MDA required conditions somewhat
347 different from those used with the basic diamines above considered. In fact, no reaction was
348 observed after 6 h at 120 °C (entry 1, Table 2). The reaction was therefore investigated in
349 the presence of a base catalyst such as DBU. In the presence of DBU, MDA reacted very
350 slowly with PC at ambient temperature (Entry 2, Table 2). A faster reaction was observed at

351

[2] The FTIR spectrum of the liquid phase (Fig. S6), after cooling the reaction mixture at ambient temperature, showed characteristic absorptions at 1684 and 1653 cm^{-1}, respectively assigned to free and associated C=O groups in ureidic oligomers [Mattia and Painter, 2007; Lortie et al., 2003; Mido, 1973].

Table 2

PC depolymerization with MDA or TDA (diamine/UR(PC) ≅1 mol/mol): synthesis of homo-polyureas MDA-PU and TDA-PU.[a]

Entry	diamine (mmol)	UR(**1**) (mmol)	THF (mL)	T (°C)	catalyst (mol%)[b]	time (h)[c]	BPA (%)[d]	PU (%)[d]
1	MDA (2.57)	2.21	25	120	-	6	[e]	[e]
2	MDA (2.61)	2.26	25	25	DBU (10.0)	64	[f]	-
3	MDA (2.59)	2.23	25	120	DBU (10.5)	27	83	MDA-PU (94)
4	MDA (2.43)	2.06	25	120	DBU (20.3)	20	84	MDA-PU (93)
5	MDA (3.09)	2.59	30	120	NaOH (15.3)	6	86	MDA-PU (89)
6	MDA (3.46)	2.99	20	120	NaOH (15.7)	6	84[g]	MDA-PU (88)
7	TDA (5.69)	4.83	30	120	NaOH (14.0)	7	95	TDA-PU (87)

[a] PC depolymerization by diamines MDA or TDA was followed by FTIR analysis of the THF solution, by monitoring over time the absorptions at 1778 cm^{-1} (due to PC) and 1715-1717 cm^{-1} (due to **1**; R = 4,4'-$C_6H_4CH_2C_6H_4$- or 2,4-C_6H_3Me, according to the used diamine (MDA or TDA)). See also 3.2 and Figs. S9 and S10.

[b] mol% relative to UR(PC).

[c] Overall reaction time.

[d] Isolated yield.

[e] No reaction.

[f] Only traces amounts of BPA were detected in the reaction mixture.

[g] Isolated by column chromatography (see Supplementary Material).

352

353 120 °C: the progress of the reaction, monitored by FTIR spectroscopy (Fig. S9), was
354 demonstrated by the decrease over time of the bands at 1778 and 1630 cm^{-1}, respectively due
355 to PC and MDA, by the temporary appearance of the absorption at 1717 cm^{-1}, due to ν(C=O) of
356 the urethanic intermediates **1** (R = 4,4'-$C_6H_4CH_2C_6H_4$-), by the growth of the bands at 1614 and
357 1593 cm^{-1} (BPA), and, finally, by the precipitation of a colorless solid isolated and characterized as
358 MDA-PU. Nevertheless, the disappearance of the bands at 1778 cm^{-1} (PC) and 1717 cm^{-1} (**1**; R =
359 4,4'-$C_6H_4CH_2C_6H_4$-) still required quite a long reaction time that depended on the DBU load (Entry

3 and 4, Table 2). The attention was, therefore, addressed to a different more effective base catalyst such as NaOH. Remarkably, a significant shortening of the depolymerization time was attained by using NaOH (15 mol%) as the catalyst of the aminolysis process (Entry 5 and 6, Table 2) in place of the amidine base. The latter catalyst was, therefore, preferred for the ureidization of TDA. In the presence of the alkali catalyst also TDA reacted effectively with PC, likewise MDA, to give the relevant polyurea TDA-PU in addition to BPA (Entry 7, Table 2).

As a whole, the above results show that PU formation by PC diaminolysis can take place quite easily under non severe conditions. The developed protocol stands out for the modest excess of the used diamine substrate relative to the polymer (in most cases ∼15 mol% versus the stoichiometric amount (diamine/UR(PC) = 1 mol/mol)). Moreover, basic diamines react with PC in the absence of any auxiliary catalyst. Actually, diamine itself can act, in principle, as the catalyst of the overall process (Fig. 7), in virtue of the well-known ability of basic amines to promote catalytically not only the aminolysis reaction of organic carbonates to carbamates [Carafa and Quaranta, 2009; Um et al., 2018] but also the aminolysis of carbamic esters to ureas [Shawali et al., 1986]. The assistance of a catalyst is required when using poorly nucleophilic amines. In this case the best results have been obtained with a commercially accessible and cheap catalyst, such as NaOH. The latter issue is not trifling as inexpensiveness is expected to be a key feature of any waste valorization process that aims at having applicative potential.

3.2.1. Spectroscopic characterization of the polyureas

The polyureas **2-7** (Fig. 7) can be isolated straightforwardly with high yield (Table 1 and 2) by filtration, once the reaction mixture was cooled to room temperature. Also BPA can be easily recovered in good yield according to conventional techniques (see Supplementary Material).

All the PUs have been characterized spectroscopically in the solid state by ATR (Figs. S11a-f), FTIR (in nujol mull; Figs. S12a-f) and CP/MAS ^{13}C NMR (Figs. S13a-f).

As a whole, the IR spectra of the isolated PUs are in excellent accordance with those reported in the literature for authentic samples of analogue polyureas prepared by different synthetic routes (Table 3). For HMDA-PU, TOTDA-PU, *m*-XYLDA-PU and *p*-XYLDA-PU the amide II band (OCN-H) can be located between 1570 and 1591 cm^{-1}, while the amide I band (ν(C=O)) and

Table 3

FTIR (in nujol mull) and ATR characteristic bands (cm^{-1}) of the isolated PUs**.**

PU	ν(N-H) ATR; FTIR	amide I ATR; FTIR	amide II ATR; FTIR	Refs.
HMDA-PU	3330; 3329	1616; 1618	1575; 1580	[Shang et al., 2012; Wu et al., 2012; Wang et al., 2016]
TOTDA-PU	3318; 3319	1611; 1614	1587; 1591	[Ying et al., 2015]
m-XYLDA-PU	3315; 3316	1622; 1622	1579; 1584	[Wu et al., 2012]
p-XYLDA-PU	3318; 3319	1614; 1614	1570; 1574	[Wu et al., 2012]
MDA-PU	3304; 3304	1641; 1641	1549; 1545	[Rockicki, 1988]
TDA-PU	3264; 3285	1637; 1639	1538; 1545	[Han et al., 2014; Li et al., 2015]

the N-H stretching (ν(N-H)) are respectively found in the ranges 1611-1622 and 3315-3330 cm^{-1} (Table 3). In the spectrum of MDA-PU (Fig. 8) and TDA-PU the above absorptions are shifted in

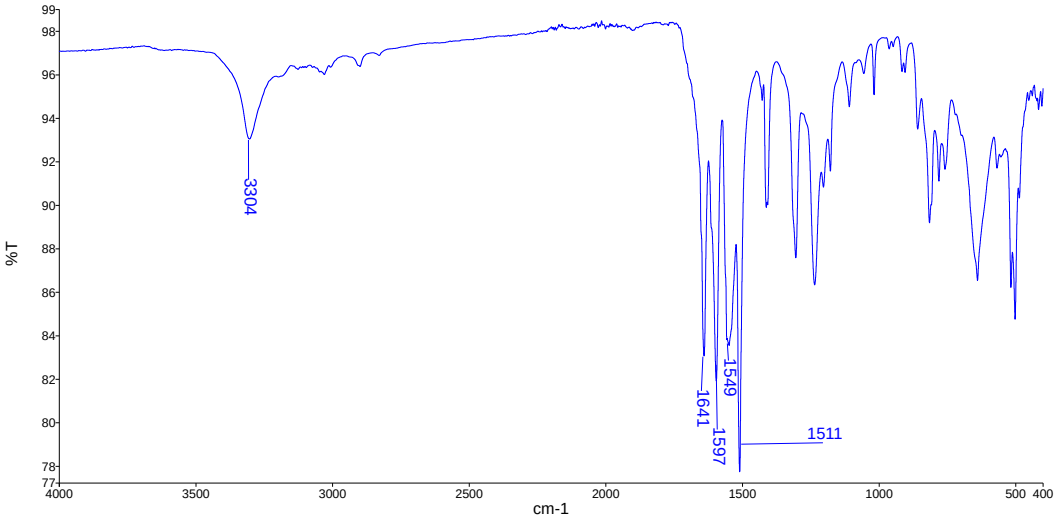


Fig. 8. ATR-FTIR spectrum of MDA-PU: IR: ν = 3304 (NH), 1641 (amide I), 1597, 1549 (amide II), 1511, cm^{-1}.

accordance with the aromatic nature of the diamine used (MDA and TDA, respectively) [Socrates, 2001]. In any case the location of the IR bands due to ν(C=O) and ν(N-H) is very informative as it supports that the carbonyl oxygen atoms and the N-H groups are involved in a strong H-bond (Fig. 9) [Li et al., 2015; He et al., 2014; Yilgor et. al., 2000; Coleman et al., 1997]. In fact, both ν(N-H) and ν(C=O) are markedly red-shifted relative to the frequency of free N-H (3450 cm^{-1}) and free C=O (1690 cm^{-1}) groups in polyureas. Moreover, the positions of ν(N-H) and ν(C=O) are typical of "hydrogen-bonded ordered" bands suggesting the presence of hydrogen-bonded groups in network structures characterized by some degree of order or regularity (Fig. 9). This may explain the high resistance of the isolated materials to common organic solvents such as hydrocarbons, aromatics, THF, diethyl ether, acetone, acetonitrile, DMF, methanol, 2-propanol. Table 4 compares the behavior of the isolated PUs in a few other solvents such as H_2O, $CHCl_3$, DMSO.

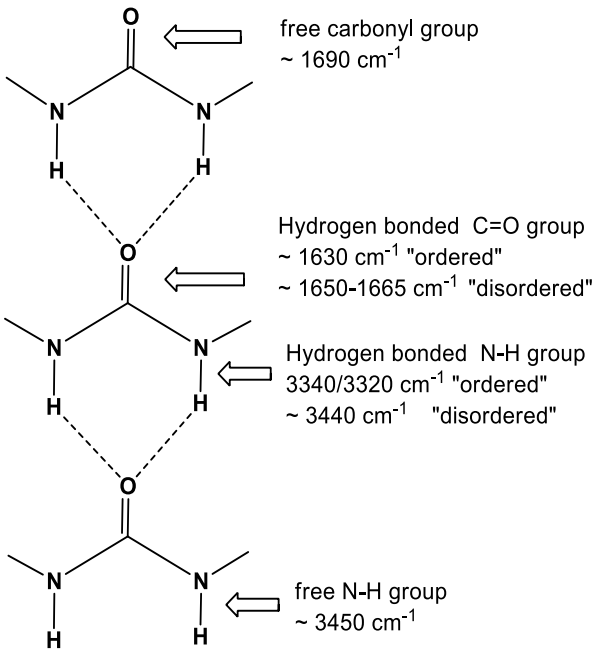


Fig. 9. Hydrogen bondings in polyureas (from ref. [Mattia and Painter, 2007]).

The polyureidic nature of the isolated products **2-7** (Fig. 7) is further supported by solid state CP/MAS ^{13}C NMR measurements (Fig. S13a-S13f and Table 5). In most cases the resonance of the ureidic carbons can be located around 160 ppm in strict accordance with the literature. In the CP/MAS ^{13}C NMR spectrum of MDA-PU (Fig. 10) the C=O resonance was found at higher field,

151.9 ppm, in accordance with the calculated value of 152.2 ppm and the experimental value (~152 ppm) found for a structurally related ureidic derivative of MDA [Aresta et al., 1998].

Table 4

Solubility behavior of the isolated PUs in a few solvents at ambient temperature (22 °C).

Solvent	HMDA-PU	TOTDA-PU	*m*-XYLDA-PU	*p*-XYLDA-PU	MDA-PU	TDA-PU
H_2O	-	+	-	-	-	-
$CHCl_3$	-	+	-	-	-	-
DMSO	-	-	-	-	-	+

"-": insoluble.

"+": soluble.

Table 5

CP/MAS ^{13}C NMR data ($\delta_{C=O}$, ppm) for the isolated polyureas.

PU	HMDA-PU	TOTDA-PU	*m*-XYLDA-PU	*p*-XYLDA-PU	MDA-PU	TDA-PU
$\delta_{C=O}$	160.7 [a]	160.0 [b]	160.0 [c]	159.0 [c]	151.9 [d,e]	157.7

[a] See also refs [Shang et al., 2012] and [Wu et al., 2012].

[b] See also ref. [Ying et al., 2015].

[c] See also ref. [Wu et al., 2012].

[d] Calculated: 152.2 ppm (software: ACD/C+H NMR Predictors and DB (v.12.01)).

[e] See also ref. [Aresta et al., 1998].

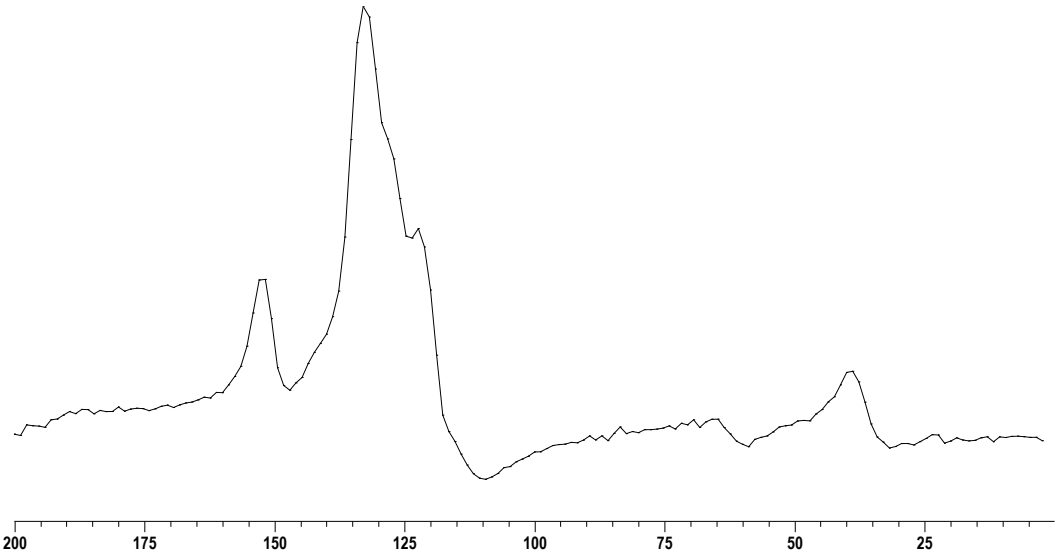


Fig. 10. CP/MAS ^{13}C-NMR (151 MHz) of MDA-PU: δ = 39.0 (CH_2), 121.3-133.1 (aromatic carbons), 151.9 (C=O) ppm.

421 The insolubility in common organic solvents has prevented, for most of the PUs synthesized,
422 any attempt of determination of molecular weights by means of traditional techniques. However,
423 because of their solubility properties (Table 4), it was possible to characterize polyureas TOTDA-
424 PU and TDA-PU by NMR spectroscopy also in solution. The NMR analysis confirmed the
425 polyureidic nature of these products, demonstrated their homogeneity, and, by means of end-group
426 analysis, allowed to estimate the degree of polymerization, providing thus a further validation of the
427 developed synthetic approaches.

428 Figs. S14 and S15 illustrate, respectively, the ^{1}H and ^{13}C NMR of TOTDA-PU in D_2O. The
429 ^{13}C NMR spectrum shows all the signals of the repeating unit of the polyurea. The ^{1}H spectrum
430 displays also additional distinguishable resonances assignable to $H_2NRNHCO$- end groups. The
431 integral proton spectrum allows to determine the number average molecular weight of TOTDA-PU
432 (M_n = 2553 Da) and to calculate the average number of repeating monomer units (n = 9.5).

433 The ^{1}H and ^{13}C NMR spectra of TDA-PU in DMSO-d_6 are reported in Figs. S16 and
434 S17, respectively. The integrals of the signals due to the NH_2 protons of the terminal TDA
435 moieties and those of all the methyl protons allow to evaluate the number of [2,4-
436 NHC_6H_3Me-NHCO-] repeating units (n = 9.6) and calculate M_n (1544 Da). In the ^{13}C NMR
437 spectrum of TDA-PU two very close resonances are found for the carbonyl carbons (152.73
438 and 152.42 ppm) that, therefore, in DMSO solution resonate at higher fields than in the solid
439 state (157.7 ppm). The analysis of the ^{13}C NMR spectrum allows to shed light on the nature
440 of the terminal group of the polymeric chains and identifies as **C** the most likely structure
441 for the end groups of the polyureidic chains (Fig. 11). This agrees well with the fact that the
442 two amino groups of TDA, that, differently from those of the other diamines considered in
443 this study, are not equivalent, exhibit a different reactivity for steric reasons, so the 4-NH_2
444 group is carbonylated more easily than that in *ortho* position to the methyl group [Aresta et
445 al., 1998; Distaso and Quaranta, 2004b].

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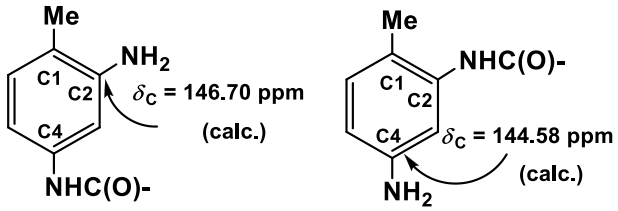

Fig. 11. Possible isomeric end-groups for TDA-PU. The carbon atom directly bound to the NH_2 group, C2 in (**C**) and C4 in (**D**), has been selected as suitable probe to distinguish between the two isomeric structures: the relevant ^{13}C nuclei, in fact, are expected to resonate at different δ_C (146.70 and 144.58 ppm; calculated with the software ACD/C+H NMR Predictors and DB (v.12.01)). For a more detailed discussion, see Supplementary Material (Fig. S17).

3.2.2. Thermal properties of the polyureas

The thermal properties of PUs **2-7** (Fig. 7) have been assessed by DSC and TGA. The second heating DSC curves are shown in Fig. 12 (left side). Only TOTDA-PU exhibits a melting behavior in the range 0-200 °C owing to the presence of ether moieties that make the polyurea structure very flexible [Dennis et al., 2018] and lower the melting temperature. The bimodal structure of the melting signals at 85.2 °C and 107.3 °C, also evident in the first heating run, is associated to different populations of lamellar crystals [Ying et al., 2015] and due to melting-recrystallization-melting phenomena [Jiang et al., 2019].[3]

The DSC curves of the other PUs show the presence of glass transitions associated to the amorphous portion of the solids. The T_g value of HMDA-PU is 54.5 °C, that falls in the T_g range 44 °C - 74 °C characteristic of polyureas with similar structure [Shang et al., 2012; Kébir et al., 2017]. *m*-XYLDA-PU undergoes glass transition at 42.4 °C, while the more symmetrical polyurea *p*-XYLDA-PU has a higher T_g value (77.6 °C). TDA-PU and MDA- PU show glass transition at 69.0 °C and 135.5 °C, respectively.

Inspection of the TGA plots, Fig. 12 (right side), performed by differential weight loss (curves not shown), reveals that only PUs TOTDA-PU and TDA-PU decomposed in one step,

[3] Only a crystallization exothermic peak at 60.2 °C was observed during the cooling run (not shown).

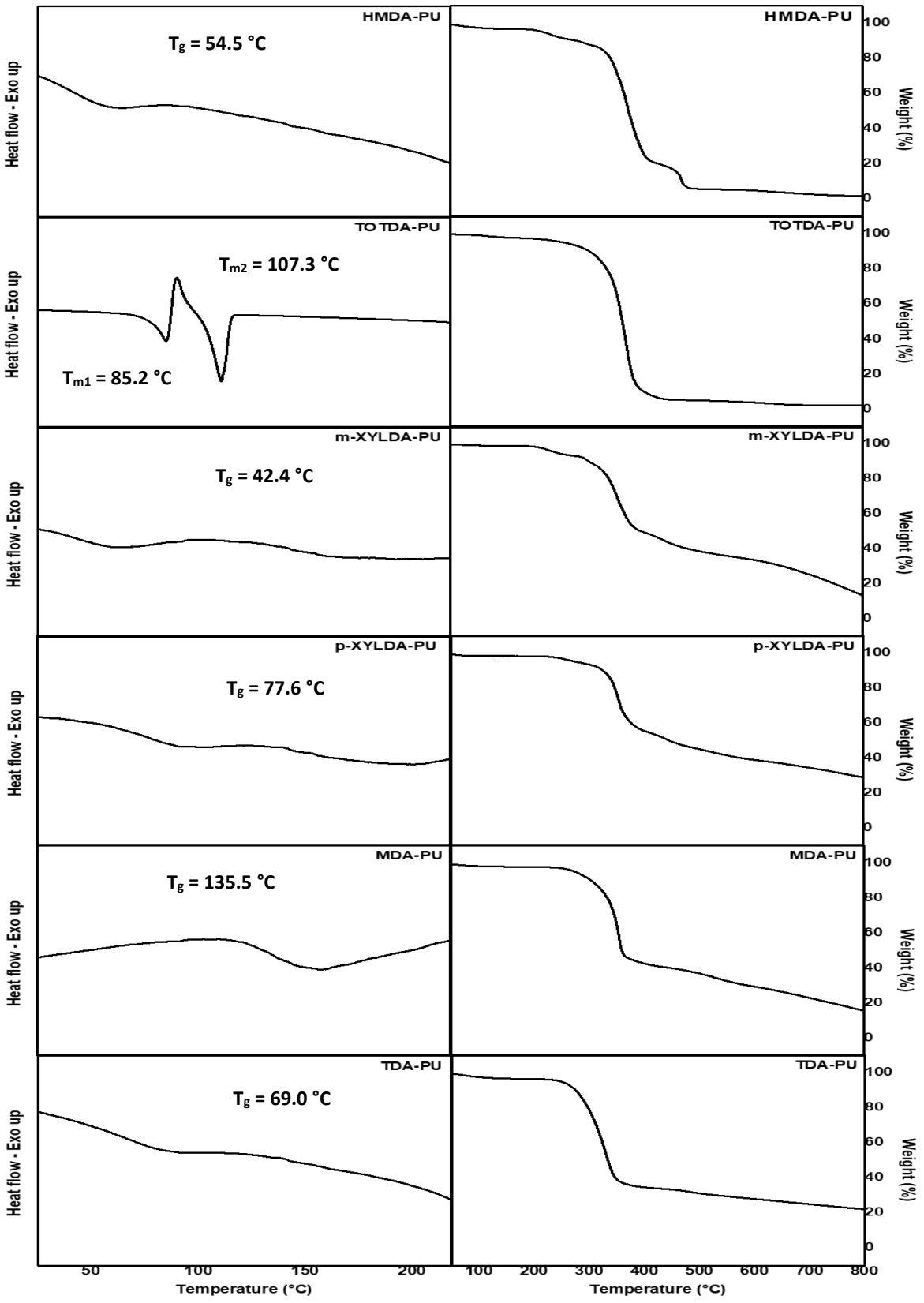

Fig. 12. DSC (left side) and TGA (right side) curves of the isolated PUs. The reported DSC curves were obtained from the second heating scan.

501 whereas all the other PUs showed a multi-stage decomposition process. The temperatures that
502 characterize the process of thermal decomposition of all the isolated PUs are reported in Table 6.

Table 6

Thermal properties of the isolated PUs measured by TGA.[a]

PU	$T_{d,5\%}$ (°C) [b]	$T_{d,½}$ (°C) [c]	$T_{d,max}$ (°C) [d]	$M_{residue}$ (%) [e]
HMDA-PU	212	368	366	2.8
TOTDA-PU	252	356	364	2.6
m-XYLDA-PU	235	390	347	25.1
p-XYLDA-PU	268	440	347	34.3
MDA-PU	270	355	349	22.8
TDA-PU	243	328	323	25.0

[a] Heating rate: 10 °C/min.

[b] Temperature at which weight loss is 5%.

[c] Temperature at which weight loss is 50%.

[d] Temperature at which the rate of decomposition is maximum.

[e] Residual weight observed at 750 °C.

503

504 The thermal stability of polyureas increases with the monomer molecular weight [Kèbir et al, 2017]
505 and depends on the polymer structure, in particular symmetry and rigidity [Esfahanizadeh et al.,
506 2015]. The presence of more rigid aromatic units along the chain leads to a general increase of
507 stability [Ban et al., 2019]. Accordingly, *m*-XYLDA-PU, *p*-XYLDA-PU, MDA-PU and TDA-PU
508 have a higher $T_{d,5\%}$ than the aliphatic HMDA-PU. Moreover, MDA-PU, with two aromatic units
509 per repeating unit, shows the highest $T_{d,5\%}$. It is worth noting that *p*-XYLDA-PU has a higher $T_{d,5\%}$
510 than *m*-XYLDA-PU as a result of the more symmetric structure, but both polyureas *m*-XYLDA-PU
511 and *p*-XYLDA-PU, having the same molecular formula, have the maximum rate of decomposition
512 at the same temperature.

513 The char residue formed after complete evaporation of the evolved species is higher for *m*-
514 XYLDA-PU, *p*-XYLDA-PU, MDA-PU and TDA-PU than for HMDA-PU and TOTDA-PU
515 because the presence of aromatic units causes an increase of the graphitization extent at high
516 temperature [Ban et al., 2019].

In summary, the thermogravimetric analysis indicates that the above PUs have high thermal stability [Ying et al., 2015] since they are stable up to 212–270 °C depending on structure, and have the maximum rate of decomposition in the range of 323-366 °C. These results are noteworthy from the practical standpoint for their applicative potential and suggest that the isolated PUs are suitable for being processed using conventional techniques since their degradation process begins at a temperature about 100 °C higher than their glass transition or melting temperature.

4. Conclusions

The reaction of poly-(bisphenol A carbonate) with either aliphatic or aromatic long-chain diamines has been explored as a way to regenerate the monomer BPA and, for the first time, to afford polyureas. The study provides an unprecedented approach to the valorization of potentially hazardous PC wastes by chemical recycling and opens a new carbon-saving synthetic entry into homo-polyureas through a non-isocyanate route.

In THF, under non severe conditions (120 °C), basic diamines, such as HMDA, TOTDA, *m*-XYLDA and *p*-XYLDA (2 equivalents), reacted with PC, without any auxiliary catalyst, to afford BPA and the relevant homo-polyureas [-NHRNHCO-]$_n$ (HMDA-PU, TOTDA-PU, *m*-XYLDA-PU and *p*-XYLDA-PU, respectively). Under otherwise analogous conditions, the conversion of the less reactive aromatic diamines MDA or TDA (2 equivalents) required the assistance of a base catalyst (NaOH, DBU).

Polyurea formation goes through a carbamation step affording BPA and intermediate urethane derivatives H-[OArOCONHRNHCO]$_n$-OArOH (**1**) (Ar = 4,4'-$C_6H_4CMe_2C_6H_4$-), that in a subsequent step convert into [-NHRNHCO-]$_n$ products and more BPA.

The developed synthetic methodology is 100% atomically economic, operationally easy, does not require any complex equipment, is characterized by high productivity and selectivity. In all the cases the depolymerization of the polymer (PC) was quantitative. Both BPA and polyureas can be isolated straightforwardly in high yield through conventional

techniques. The thermal properties ($T_{d,5\%}$, $T_{d,1/2}$, T_g, T_m) of HMDA-PU, TOTDA-PU, *m*-XYLDA-PU, *p*-XYLDA-PU, MDA-PU and TDA-PU, measured by DSC and TGA, make these materials suitable for being processed.

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Conflict of interest

The authors declare no conflict of interest.

Appendix A (Supplementary Data)

Supplementary material related to this article is available as a separate file.

References

Alberti, C., Kessler, J., Eckelt, S., Hofmann, M., Kindler, T.O., Santangelo, N., Fedorenko, E. Enthaler, S., 2020a. Hydrogenative Depolymerization of End-of-Life Poly(bisphenol A carbonate) with in situ Generated Ruthenium Catalysts. ChemistrySelect 5, 4231-4234. https://doi.org/10.1002/slct.202000626.

Alberti, C., Enthaler, S., 2020b. Depolymerization of End-of-Life Poly(bisphenol A carbonate) via Alkali-Metal-Halide-Catalyzed Methanolysis. Asian J. Org. Chem. 9, 359-363. https://doi.org/10.1002/ajoc.201900242.

Alberti, C., Scheliga, F., Enthaler, S., 2019. Recycling of End-of-Life Poly(bisphenol A carbonate) via Alkali Metal Halide-Catalyzed Phenolysis. ChemistryOpen 8, 822–827. https://doi.org/10.1002/open.201900149.

Antonakou, E.V., Achilias, D.S., 2013. Recent advances in polycarbonate recycling: A review of degradation methods and their mechanisms. Waste Biomass Valori. 4, 9-21. https://doi.org/10.1007/s12649-012-9159-x.

Aresta, M., Berloco, C., Quaranta, E., 1995. Biomimetic building-up of the carbamic moiety: the intermediacy of carboxyphosphate analogues in the synthesis of N-aryl carbamate esters from arylamines and organic carbonates promoted by phosphorous acids. Tetrahedron. 51, 8073-8088. https://doi.org/10.1016/0040-4020(95)00424-7.

579 Aresta, M., Dibenedetto, A., Quaranta, E., 1998. Reaction of aromatic diamines with diphenyl
580 carbonate catalyzed by phosphorous acids: a new clean synthetic route to mono- and dicarbamates.
581 Tetrahedron. 54, 14145-14156. https://doi.org/10.1016/S0040-4020(98)00873-4.
582
583 Aresta, M., Dibenedetto, A., Quaranta, E., 1999. Selective carbomethoxylation of aromatic
584 diamines with mixed carbonic acid diesters in the presence of phosphorous acids. Green Chem. 1,
585 237-242. https://doi.org/10.1039/A904624K.
586
587 Asscoated Press News, 2018. https://apnews.com/0251b75ab0de4d3080214e95a57bf0ee (accessed
588 27 May 2020).
589
590 Ban, J., Li, S., Yi, C., Zhao, J., Zhang, Z., Zhang, J., 2019. Amorphous and Crystallizable
591 Thermoplastic Polyureas Synthesized through a One-pot Non-isocyanate Route. Chin. J. Polym.
592 Sci. 37, 43–51. https://doi.org/10.1007/s10118-018-2165-0.
593
594 Carafa, M., Quaranta, E., 2009. Synthesis of Organic Carbamates without Using Phosgene:
595 Carbonylation of Amines with Carbonic Acid Diesters. Mini-Rev. Org. Chem. 6, 168-183.
596 https://doi.org/10.2174/157019309788922720.
597
598 Coleman, M.M., Sobkowiak, M., Pehlert, G.J., Painter, P.C., Iqbal, T., 1997. Infrared temperature
599 studies of a simple polyurea. Macromol. Chem. Phys. 198, 117-136.
600 https://doi.org/10.1002/macp.1997.021980110.
601
602 Datta, J., Kopczynska, P., 2016. From polymer waste to potential main industrial products: Actual
603 state of recycling and recovering. Crit. Rev. Environ. Sci. Technol. 46, 905-946.
604 https://doi.org/10.1080/10643389.2016.1180227.

605 Demarteau, J., O'Harra, K.E., Bara, J.E., Sardon, H., 2020. Valorization of Plastic Wastes for the
606 Synthesis of Imidazolium-Based Self-Supported Elastomeric Ionenes. ChemSusChem 13, 3122-
607 3126. https://doi.org/10.1002/cssc.202000505.
608
609 Dennis, J.M., Steinberg, L.I., Pekkanen, A.M., Maiz, J., Hegde, M., Muller, A.J., Long, T.E., 2018.
610 Synthesis and Characterization of Isocyanate-free Polyureas. Green Chem. 20, 243-249.
611 https://doi.org/10.1039/C7GC02996A.
612
613 Distaso, M., Quaranta, E., 2004a. Group 3 metal (Sc, La) triflates as catalysts for the
614 carbomethoxylation of aliphatic amines with dimethylcarbonate under mild conditions.
615 Tetrahedron. 60, 1531. https://doi.org/10.1016/j.tet.2003.12.020.
616
617 Distaso, M., Quaranta, E., 2004b. Carbomethoxylating reactivity of methyl phenyl carbonate toward
618 aromatic amines in the presence of group 3 metal (Sc, La) triflate catalyst. J. Catal. 228, 36-42.
619 https://doi.org/10.1016/j.jcat.2004.08.004.
620
621 Distaso, M., Quaranta, E., 2006. Highly selective carbamation of aliphatic diamines under mild
622 conditions using $Sc(OTf)_3$ as catalyst and dimethyl carbonate as a phosgene substitute. Appl. Catal.
623 B Environ. 66, 72-80. https://doi.org/10.1016/j.apcatb.2006.02.019.
624
625 Do, T., Baral, E.R., Kim, J.G., 2018. Chemical recycling of poly(bisphenol A carbonate): 1,5,7-
626 Triazabicyclo[4.4.0]-dec-5-ene catalyzed alcoholysis for highly efficient bisphenol A and organic
627 carbonate recovery. Polymer. 143, 106–114. https://doi.org/10.1016/j.polymer.2018.04.015.
628

629 Esfahanizadeh, M., Sabbaghian, E., Mehdipour-Ataei, S., Jalilian, S., Babanzadeh, S., 2015.
630 Synthesis and Characterization of New Polyureas with Improved Thermal Stability from a Novel
631 Ether Keto Diamine. Adv. Polym. Technol. 34, 21511. https://doi.org/10.1002/adv.21511.
632
633 Fortman, D.J., Brutman, J.P., De Hoe, G.X., Snyder, R.L., Dichtel, W.R., Hillmyer, M.A., 2018.
634 Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers. ACS Sustainable
635 Chem. Eng. 6, 11145-11159. https://doi.org/10.1021/acssuschemeng.8b02355.
636
637 Han, H., Li, S., Zhu, X., Jiang, X., Kong, X.Z., 2014. One step preparation of porous polyurea by
638 reaction of toluene diisocyanate with water and its characterization. RSC Adv. 4, 33520–33529.
639 https://doi.org/10.1039/C4RA06383J.
640
641 Hata, S., Goto, H., Yamada, E., Oku, A., 2002. Chemical conversion of polycarbonate to 1,3-
642 dimethyl-2-imidazolidinone (DMI) and bisphenol A: a practical approach to the chemical recycling
643 of plastic wastes. Polymer. 43, 2109-2116. https://doi.org/10.1016/S0032-3861(01)00800-X.
644
645 Hata, S., Goto, H., Tanaka, S., Oku, A., 2003. Viable Utilization of Polycarbonate as a Phosgene
646 Equivalent Illustrated by Reactions with Alkanedithiols, Mercaptoethanol, Aminoethanethiol, and
647 Aminoethanol: A Solution for the Issue of Carbon Resource Conservation. J. Appl. Polym. Sci. 90,
648 2959-2968. https://doi.org/10.1002/app.12936.
649
650 He, Y., Xie, D., Zhang, X., 2014.The structure, microphase-separated morphology, and property of
651 polyurethanes and polyureas. J. Mater. Sci. 49, 7339-7352. https://doi.org/10.1007/s10853-014-
652 8458-y.
653

Hong, M., Chen, E.Y.-X., 2017. Chemically Recyclable Polymers: A Circular Economy Approach to Sustainability. Green Chem. 19, 3692–3706. https://doi.org/10.1039/C7GC01496A.

Iannone, F., Casiello, M., Monopoli, A., Cotugno, P., Sportelli, M.C., Picca, R.A., Cioffi, N., Dell'Anna, M.M., Nacci, A., 2017. Ionic liquids/ZnO nanoparticles as recyclable catalyst for polycarbonate depolymerization. J. Mol. Catal. A Chem. 426, 107-116. https://doi.org/10.1016/j.molcata.2016.11.006.

Jehanno, C., Pérez-Madrigal, M.M., Demarteau, J., Sardon, H., Dove, A.P., 2019. Organocatalysis for depolymerisation. Polym. Chem. 10, 172-186. https://doi.org/10.1039/C8PY01284A.

Jehanno, C., Demarteau, J., Mantione, D., Arno, M.C., Ruipérez, F., Hedrick, J.L., Dove, A.P., Sardon, H., 2020. Synthesis of Functionalized Cyclic Carbonates through Commodity Polymer Upcycling. ACS Macro Lett. 9, 443-447. https://doi.org/10.1021/acsmacrolett.0c00164.

Jiang, S., Cheng, H., Shi, R., Wu, P., Lin, W, Zhang, C., Arai, M., Zhao, F., 2019. Direct Synthesis of Polyurea Thermoplastics from CO_2 and Diamines. ACS Applied Materials & Interfaces 11 (50), 47413-47421. https://doi.org/10.1021/acsami.9b17677.

Jones, G.O., Yuen, A., Wojtecki, R.J., Hedrick, J.L., Garcia, J.M., 2016. Computational and experimental investigations of one-step conversion of poly(carbonate)s into value-added poly(aryl ether sulfone)s. Natl. Acad. Sci. U. S. A. 28, 7722-7726. https://doi.org/10.1073/pnas.1600924113.

Kébir, N., Benoit, M., Legrand, C., Burel, F., 2017. Non-isocyanate thermoplastic polyureas (NIPUreas) through a methyl carbamate metathesis polymerization. Eur. Polym J. 96, 87-96. https://doi.org/10.1016/j.eurpolymj.2017.08.046.

680 Kim, J.G., 2020. Chemical recycling of poly(bisphenol A carbonate). Polym. Chem.
681 https://doi.org/10.1039/C9PY01927H.
682
683 La Mantia, F. (Ed.), 2002. Handbook of Plastic Recycling. Rapra Technology, Shrewsbury, U.K.
684
685 Li, S., Han, H., Zhu, X., Jiang, X., Kong, X.Z., 2015. Preparation and Formation Mechanism of
686 Porous Polyurea by Reaction of Toluene Diisocyanate with Water and Its Application as Adsorbent
687 for Anionic Dye Removal. Chinese J. Polymer Sci. 33, 1196-1210. https://doi.org/10.1007/s10118-
688 015-1670-7.
689
690 Liu, M., Guo, J., Gu, Y., Gao, J., Liu, F., 2018. Degradation of waste polycarbonate via hydrolytic
691 strategy to recover monomer (bisphenol A) catalyzed by DBU-based ionic liquids under metal- and
692 solvent-free conditions. Polym. Degrad. Stab. 157, 9-14.
693 https://doi.org/10.1016/j.polymdegradstab.2018.09.018.
694
695 Liu, F., Guo, J., Zhao, P., Jia, M., Liu, M., Gao, J., 2019. Novel succinimide-based ionic liquids as
696 efficient and sustainable media for methanolysis of polycarbonate to recover bisphenol A (BPA)
697 under mild conditions. Polym. Degrad. Stab. 108996.
698 https://doi.org/10.1016/j.polymdegradstab.2019.108996.
699
700 Lortie, F., Boileau, S., Bouteiller, L., 2003. N,N-Disubstituted Ureas: Influence of Substituents on
701 the Formation of Supramolecular Polymers. Chem. Eur. J. 9, 3008 – 3014 and refs therein.
702 https://doi.org/10.1002/chem.200304801.
703

704 Ma, S., van Heeswijk, E.P.A., Noordover, B.A.J., Sablong, R.J., van Benthem, R.A.T.M., Koning,
705 C.E., 2018. Isocyanate-Free Approach to Water-Borne Polyurea Dispersions and Coatings.
706 ChemSusChem. 11, 149-158. https://doi.org/10.1002/cssc.201701930.
707
708 Mattia, J., Painter, P., 2007. A comparison of hydrogen bonding and order in a polyurethane and
709 poly(urethane-urea) and their blends with poly(ethytlene glycol). Macromolecules. 40, 1546-1554.
710 https://doi.org/10.1021/ma0626362.
711
712 Mido, Y., 1972. Infrared spectra and configurations of dialkylureas. Spectrochimica Acta. 28A,
713 1503-1518. https://doi.org/10.1016/0584-8539(72)80120-X.
714
715 Mido, Y., 1973. An infrared study of various dialkylureas in solution. Spectrochimica Acta. 29A,
716 431-438. https://doi.org/10.1016/0584-8539(73)80025-X.
717
718 Monsigny, L., Berthet, J.-C., Cantat, T., 2018. Depolymerization of Waste Plastics to Monomers
719 and Chemicals Using a Hydrosilylation Strategy Facilitated by Brookhart's Iridium(III) Catalyst.
720 ACS Sustainable Chem. Eng. 6, 10481-10488. https://doi.org/10.1021/acssuschemeng.8b01842.
721
722 Pan, W.C., Liao, K., Lin, C.-H., Dai, S.A., 2015. Solvent-free processes to polyurea elastomers
723 from diamines and diphenyl carbonate. J. Polym. Res. 22, 114. https://doi.org/10.1007/s10965-
724 015-0747-x.
725
726 Perrin, D.D., Armarego, W.L.F., Perrin, D.R., 1986. Purification of Laboratory Chemicals.
727 Pergamon, Oxford.
728

729 Pires, R.F., Bonifacio, V.D.B., 2000. Polyureas, in: Kirk-Othmer Encyclopedia of Chemical
730 Technology. John Wiley & Sons, Inc. https://doi.org/10.1002/0471238961.koe00032.
731
732 Quaranta, E., 2017. Rare Earth metal triflates $M(O_3SCF_3)_3$ (M = Sc, Yb, La) as Lewis acid catalysts
733 of depolymerization of poly-(bisphenol A carbonate) via hydrolytic cleavage of carbonate moiety:
734 Catalytic activity of $La(O_3SCF_3)_3$. Appl. Catal. B Environ. 206, 233-241.
735 https://doi.org/10.1016/j.apcatb.2017.01.007.
736
737 Quaranta, E., Sgherza, D., Tartaro, G., 2017. Depolymerization of poly(bisphenol A carbonate)
738 under mild conditions by solvent free alcoholysis catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene
739 as a recyclable organocatalyst: a route to chemical recycling of waste polycarbonate. Green Chem.
740 19, 11-16. https://doi.org/10.1039/C7GC02063E.
741
742 Quaranta, E., Castiglione Minischetti, C., Tartaro, G., 2018. Chemical recycling of poly(bisphenol
743 A carbonate) by glycolysis under 1,8-diazabicyclo[5.4.0]undec-7-ene catalysis. ACS Omega 3,
744 7261-7268. https://doi.org/10.1021/acsomega.8b01123.
745
746 Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic
747 waste. Waste Manage. 69, 24–58. https://doi.org/10.1016/j.wasman.2017.07.044.
748
749 Rahimi, A.R., García, J.M., 2017. Chemical recycling of waste plastics for new materials
750 production. Nat. Rev. Chem. 1, 41570-41580. https://doi.org/10.1038/s41570-017-0046.
751
752 Rokicki, G., 1988. Direct method of synthesis of polyureas by N-acylphosphoramidites. Makromol.
753 Chem. 189, 2513-2520. https://doi.org/10.1002/macp.1988.021891101.

754 Shang, J., Liu, S., Ma, X., Lua, L., Deng, Y., 2012. A new route of CO_2 catalytic activation:
755 syntheses of N-substituted carbamates from dialkyl carbonates and polyureas. Green Chem. 14,
756 2899-2906. https://doi.org/10.1039/C2GC36043H.
757
758 Shao, S.W., Chen, H.C., Chan, J.R., Juang, T.Y., Abu-Omar, M.M., Lin, C.H., 2020. Full atom-
759 efficiency transformation of wasted polycarbonates into epoxy thermosets and the catalyst-free
760 degradation of the thermosets for environmental sustainability. Green Chem. 22, 4683-4696.
761 https://doi.org/10.1039/d0gc01318h.
762
763 Shawali, A.S., Harhash, A., Sidky, M.M., Hassaneen, H.M., Elkaabi, S.S., 1986. Kinetics and
764 Mechanism of Aminolysis of Carbamates. J. Org. Chem. 51, 3498-3501.
765 https://doi.org/10.1021/jo00368a020.
766
767 Singh, S., Leib, Y., Schober, A., 2015. Direct extraction of carbonyl from waste polycarbonate
768 with amines under environmentally friendly conditions: scope of waste polycarbonate as a
769 carbonylating agent in organic synthesis. RSC Adv. 5, 3454-3460.
770 https://doi.org/10.1039/C4RA14319A.
771
772 Socrates, G., 2001. Infrared and Raman Characteristic Group Frequencies, third ed. John Wiley &
773 Sons, LTD, Chichester, England, pp. 151-154.
774
775 Taguchi, M., Ishikawa, Y., Kataoka, S., Naka, T., Funazukuri, T., 2016. CeO_2 nanocatalysts for the
776 chemical recycling of polycarbonate. Catal. Commun. 84, 93-97.
777 https://doi.org/10.1016/j.catcom.2016.06.009.
778

779 Tang, H., Hu, T., Li, G., Wang, A., Xu, G., Yu, C., Wang, X., Zhang, T., Li, N., 2019. Synthesis of
780 jet fuel range high-density polycycloalkanes with polycarbonate wast. Green Chem. 21, 3789-3795.
781 https://doi.org/ 10.1039/c9gc01627a.
782
783 Tucker, D.K., Hayes Bouknight, S., Brar, S.S., Kissling G.E., Fenton, S.E., 2018. Evaluation of
784 Prenatal Exposure to Bisphenol Analogues on Development and Long-Term Health of the
785 Mammary Gland in Female Mice. Environ. Health Perspect. 126, 087003.
786 https://doi.org/10.1289/EHP3189.
787
788 Um, I.-H., Song, J.-H., Bae, A.-R., Dust, J.M., 2018. Unexpected medium effect on the mechanism
789 for aminolysis of aryl phenyl carbonates in acetonitrile and H_2O: transition-state structure in the
790 catalytic pathway. Can. J. Chem. 66, 1011-1020. https://doi.org/10.1139/cjc-2018-0204.
791
792 Wang, P., Ma, X., Li, Q., Yang, B., Shang, J., Deng, Y., 2016. Green synthesis of polyureas from
793 CO_2 and diamines with a functional ionic liquid as the catalyst. RSC Adv. 6, 54013-54019.
794 https://doi.org/10.1039/C6RA07452A.
795
796 Wang, J., Jiang, J., Wang, X., Wang, R., Wang, K., Pang, S., Zhong, Z., Sun, Y., Ruan, R.,
797 Ragauskas, A.J., 2020. Converting polycarbonate and polystyrene plastic wastes into aromatic
798 hydrocarbons via catalytic fast co-pyrolysis. J. Hazard. Mater. 386, 121970.
799 https://doi.org/10.1016/j.jhazmat.2019.121970.
800
801 Westhues, S., Idel, J., Klankermayer, J., 2018. Molecular catalyst systems as key enablers for
802 tailored polyesters and polycarbonate recycling concepts. Sci. Adv. 4(8), eaat9669.
803 https://doi.org/10.1126/sciadv.aat9669.
804

Wu, C., Wang, J., Chang, P., Cheng, H., Yu, Y., Wu, Z., Dong, D., Zhao, F., 2012. Polyureas from diamines and carbon dioxide: synthesis, structures and properties. Phys. Chem. Chem. Phys. 14, 464–468. https://doi.org/10.1039/C1CP23332G.

Wu, C.-H., Chen, L.-Y., Jeng, R.-J., Dai, S.A., 2018. 100% Atom-economy efficiency of recycling polycarbonate into versatile intermediates. ACS Sustainaible Chem. Eng. 6, 8964-8975. https://doi.org/10.1021/acssuschemeng.8b01326.

Yilgor, E., Burgaz, E., Yurtsever, E., Yilgor, I., 2000. Comparison of hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea copolymers. Polymer. 41, 849–857. https://doi.org/10.1016/S0032-3861(99)00245-1.

Ying, Z., Zhao, L., Zhang, C., Yu, Y., Liu, T., Cheng, H., Zhao, F., 2015. Utilization of carbon dioxide to build a basic block for polymeric materials: an isocyanate-free route to synthesize a soluble oligourea. RSC Adv. 5, 42095–42100. https://doi.org/10.1039/C5RA02819A.