# The organic chemistry behind the recycling of poly(bisphenol-A carbonate) for the preparation of chemical precursors: A review

**Elangeni Ana Gilbert**[1] | **Mara Lis Polo**[1] | **Juan Martín Maffi**[2] | **Javier Fernando Guastavino**[1] | **Santiago Eduardo Vaillard**[1] | **Diana Alejandra Estenoz**[1] (ORCID)

[1]Instituto de Desarrollo Tecnológico para la Industria Química, INTEC (Universidad Nacional del Litoral - CONICET), Santa Fe, Argentina

[2]Instituto Tecnológico de Buenos Aires (ITBA), Buenos Aires, Argentina

**Correspondence**

Santiago Eduardo Vaillard, Instituto de Desarrollo Tecnológico para la Industria Química, INTEC (Universidad Nacional del Litoral - CONICET), Güemes 3450, C.P. S3000GLN, Santa Fe, Argentina.
Email: svaillard@intec.unl.edu.ar

Diana Alejandra Estenoz, Instituto de Desarrollo Tecnológico para la Industria Química, INTEC (Universidad Nacional del Litoral - CONICET), Güemes 3450, C.P. S3000GLN, Santa Fe, Argentina.
Email: destenoz@santafe-conicet.gov.ar

**Abstract**

Production and consumption of poly(bisphenol-A carbonate) resins are seeing a worldwide increase. However, their usage lifetimes are short and their final disposition as landfills pose environmental and health risks, due to the release of toxic bisphenol-A (BPA). The development of alternative recycling routes is thus becoming subject of increasing interest. In this review, the main recycling processes of poly(bisphenol-A carbonate) are described and critically compared, with special focus on the chemical mechanisms. While mechanical recycling is possible, the end products are restricted only to polymer blends, whose main mechanical properties decrease with each compounding cycle. In turn, chemical recycling can produce BPA monomer and a variety of by-products that can be used in different industries, including the polymeric field, as synthesis reagents and precursors. The operation conditions of each method are reviewed, as well as the different results obtained in terms of product yield, composition, selectivity and reaction times. Reaction mechanisms are described in detail and a view on the usability of each end product is offered.

**KEYWORDS**

bisphenol a, chemical recycling, polycarbonate, pyrolysis

## 1 | INTRODUCTION

Aromatic polycarbonate (PC) resins are widely used engineering thermoplastics, unlike their aliphatic counterparts, which have few industrial applications.[1] By far, the most widely used PC is poly(bisphenol-A carbonate) (PC-BPA), whose market size was estimated at USD 15.24 billion in 2015—with a global demand of 4.3 million tons—and is expected to reach USD 25.37 billion by 2024—increasing its demand to 7.7 million tons.[2]

The toughness and impact strength of this material, together with its chemical resistance to water and some solvents, make it a good candidate for several applications, including electrical insulations, power plugs, household appliances, automobile parts, office equipment, and packaging. Transparent grades are also used in the construction sector as window panes and roofs of different building types.[3] Packaging applications are uncommon due to the toxicity of BPA (except in baby bottles and related products where this material is firmly banned).[4]

The industrial manufacturing process of PC-BPA consists of a heterogeneous polymerization of BPA (in methyl chloride solution) and phosgene (gas), in the presence of water (in which by-product NaCl is concentrated) and a tertiary amine that acts as a catalyst.[5] Sodium hydroxide is used to ensure a pH of 10–12. The general reaction is shown in Scheme 1.

The obtained polymer is washed first with an acid (to remove basic residues) and then with water. While this is the most popular approach, the use of toxic raw materials like BPA and phosgene has promoted researchers to explore alternative routes that avoid such compounds. A review of the techniques that replace phosgene with $CO_2$ was reported recently, as were some advances in BPA-free routes.[6–8] However, the scale-up of these processes is still challenging from a technological viewpoint.

The growth of the PC industry comes with an unsettling downside: life duration is very short and its natural degradation, extremely slow.[9] Final deposition as landfill material or incineration is increasingly costly or inconvenient (since it may leach BPA into the environment), and millions of tons end up in soils and oceans, producing a major pollution problem.[10–13] Therefore, considering both the hazardous raw materials and the short lifespan of the product, recycling and reusing seem to be an optimal solution to the environmental problem that the manufacturing of PC represents.

Although local plastic recycling is encouraged, it is a world-wide market: Europe exported 2 billion tons of plastic waste to China in 2017, and new importers are emerging in South-East Asia.[13] According to Tsintzou and co-workers, there exist four main recycling methods[14]:

1. *Primary recycling*: which takes place in-plant and reuses the scrap material of known and controlled properties. It is a simple, low-cost recycling of clean waste.
2. *Mechanical recycling*: after separating the polymer from its contaminants, it is processed by melt extrusion into granules. Even if the main polymer is not modified during this process, its properties may deteriorate over each cycle.
3. *Chemical recycling*: by partial or total depolymerization, the material is transformed into oligomers and other chemical substances, which could be potentially used to regenerate the original polymer. Thermochemical methods, such as pyrolysis, are also included in this category.

4. *Energy recovery*: while considered a "recycling" of the energy content of the polymer chains[15] (in alignment with ASTM D7209-06 standard definition), it is strictly a valorization method. Due to the health risks associated with the release of toxic gases, it has been considered an unacceptable route. It is usually chosen when recycling is not possible due to constraints.[16]

In the recent years, the fifth method has become of interest:

5. *Biological recycling*: using bacteria, fungi and other microorganisms, some polymers may be degraded down to oligomers or other substances. Some of the resulting products could be used to regenerate the polymer and some others can be used as compost.[17]

Reconverting waste plastic into new raw materials by a mechanical method (perhaps the most widespread of all) usually comprises several steps, including[18]:

- Sorting: based on shape and size, color, density and/or chemical composition.
- Washing: with the aim of removing any superficial contaminants.
- Grinding and (optionally) compounding: reducing the plastic into granules for ease of transport and handling.
- Reprocessing: after compounding (usually by extrusion), with a processing technique suitable for the polymer type (extrusion molding, injection molding, roll pressing, blow molding, etc.).

Separation techniques include manual separation, flotation,[19] froth flotation (for polymers with the similar densities), and magnetic density separation.[20,21] Advances using microwave irradiation for hydrophilicity modification were reviewed recently, and specifically applied to the separation by flotation of PC mixtures with other polymers.[22,23] Regarding the recycling procedure, a common route is to produce polymer mixtures to enhance the properties of a given material. In this sense, two typical strategies are usually identified to treat mixtures of plastic waste: (i) mixing and compatibilization followed by compression molding; and (ii) compounding by extrusion followed by injection-molding of extruded pellets.[24] A typical mechanical recycling process diagram is shown in Scheme 2, taken from Francés and co-workers.[25]
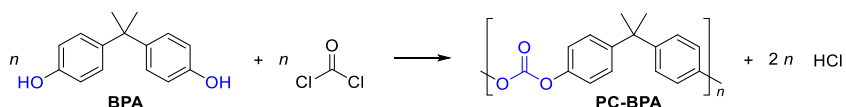
**SCHEME 1**    PC-BPA synthesis
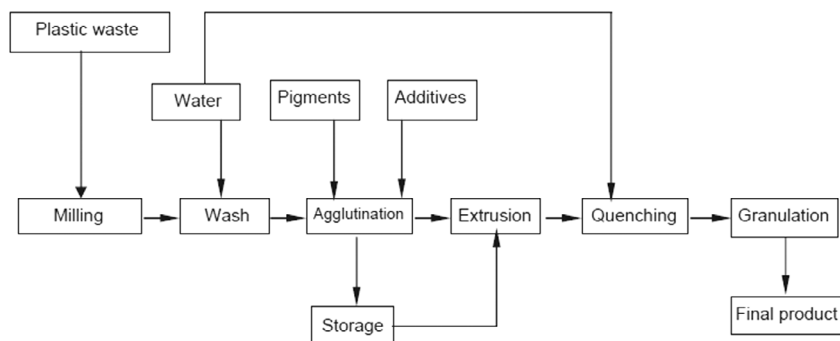
SCHEME 2  Typical recycling process diagram for plastic materials

While mechanical recycling is possible for PC-BPA, it is far less frequent than for other polymeric materials, such as polyethylene terephthalate (PET). The main reason is that PC products are not code-tagged in the international recycling system. Instead, the chemical methods offer a wider range of possibilities. Both PET and PC-BPA may be recycled chemically, but the former generally requires less energy and may be fully depolymerized in 2 h under optimized conditions.[26] In consequence, studying the chemical recycling routes for PC-PBA and how to optimize them is of current interest.

The differences between the possible chemical routes arise not only from their intrinsic kinetic mechanism, but also from their end-products separation processes. Pyrolysis techniques usually produce a mixture of gas and liquid compounds, which may be easily separated by gravity and then further processed by distillation.[14] Other techniques that use additional reagents (hydrogenolysis, hydrolysis, alcoholysis, aminolysis, and thiolysis), require the presence of organic solvents that makes the final products difficult to separate, which increases their cost and their environmental/safety problems.[1] Complex liquid–liquid extraction or crystallization (dissolution/precipitation) techniques are needed in those cases. A thorough review of these differences was published recently by Ni and co-workers.[27]

Regarding the chemical methods for the recycling of PC-BPA, a review of several routes was reported recently by Kim.[28] However, a detailed analysis of the reaction paths as well as a thorough description of the different end products that may be obtained is still lacking. In this work, the chemical recycling methods of PC-BPA are discussed critically, focusing mainly on the variety of products that may be obtained. The following is a discussion of the most promising recycling methods of PC-BPA, including pyrolysis, hydrogenation, hydrolysis, alcoholysis, aminolysis, and thiolysis.

# 2 | THERMOCHEMICAL RECYCLING BY PYROLYSIS

The thermochemical decomposition of polymers has been studied for more than 50 years, and is still a promising recycling process since hydrocarbon-based fuels and different useful chemicals could be obtained from the disposed polymers.[29,30] Pyrolysis is a chemical process where polymer molecules are degraded into low molar mass organic compounds via thermochemical decomposition.[28,31,32] The process requires elevated temperatures (300–1000°C) and an inert atmosphere for short periods of time, since the absence of oxygen produces a thermal fragmentation of the organic compounds instead of a combustion.[28,33] The products generated during pyrolysis include gas, liquid oil, and solid char fractions.[32] The gas produced is a mixture of different low molar mass hydrocarbons with high calorific capacities (typically 22–30 MJ m$^{-3}$), that can be employed as fuel in gas engines or boilers.[1] The liquid fraction can also be used as fuel or, more interestingly, as precursors for the synthesis of different chemicals or polymers.[1] Finally, the solids obtained are the reactor residues and can be used in thermal processes.[1] The products' yield and composition depend on different process parameters, such as polymer feed, type of reactor and operating conditions (pressure, temperature, heating rate, residence time, and the presence of catalyst and type).[1,34]

Pyrolysis can be carried out via thermal (or non-catalytic) or thermal-catalytic routes. Thermal-catalytic pyrolysis tries to overcome the disadvantages of thermal pyrolysis, by lowering the process temperature and reaction time, and/or narrowing the products distribution.

## 2.1 | Thermal pyrolysis

The thermal decomposition of PC has been experimentally and theoretically investigated since the 1960s.[30,35–64] In general, these articles discussed the mechanism and reaction kinetics involved in the thermal decomposition—including pyrolysis—of PC.[35–57] However, only few studies have focused on quantifying the chemical composition of the different fractions obtained at the end of the pyrolysis reaction.[30,58–64]

### 2.1.1 | Thermal decomposition mechanism

Even though thermal decomposition of PC has been studied for more than 50 years, there is still some controversy regarding the degradation mechanism involved in this process, which could be related to differences in the physical nature and properties of the polymer, in the reactor configuration, and in the reaction conditions; which all lead to differences in products structure and composition.

The first study regarding the thermal decomposition of PC-BPA was reported by Lee, who suggested that—in presence of oxygen and in vacuum—three main steps could be considered.[35] The initial step is an oxidation of the isopropylidene linkage by homolytic cleavage at temperatures above 310°C, generating water and hydroxyl compounds. Then, the second step involves depolymerization reactions that decrease the molar mass distribution. Depolymerization involve the following reactions: (i) hydrolysis—generating carbon dioxide, shorter polymer chains with hydroxyl end groups and BPA; and (ii) alcoholysis—generating shorter polymer chains with carbonate and hydroxyl end groups. At temperatures above 500°C occurs the majority of the weight loss, and the third step of thermal degradation could be considered. At this stage, random chain scissions become important, although other reaction could occur—such as decarboxylation, dehydration, hydrolysis, hydrogen abstraction, ether cleavage, and crosslinking.

Later, Davis and Golden studied the thermal degradation of several PCs, and proposed a balanced competition between crosslinking and random scission of the carbonate linkage, respectively caused by condensation and hydrolysis reactions.[36] Scission reactions predominate when the volatile products are retained in the system, while crosslinking reactions are favored when volatiles are eliminated. In further studies, Davis and Golden postulated that homolytic scission of isopropylidene linkage also occurs at a minor extent in the thermal degradation of PC-BPA.[37] Similarly, Bartosiewicz and Booth[38] studied the thermal degradation of a PC-BPA under continuous vacuum, and obtained results consistent with those published by Davis and Golden.[36] In this direction, Abbås reported that the scission is present during PC-BPA thermal degradation but it does not follow a random process.[39]

However, other authors suggested that the main degradation pathway for different PCs consists of a number of ionic mechanisms, such as the rearrangement of the carbonate linkages based on intramolecular ester exchange and the disproportionation of isopropylidene linkages, followed by decarboxylation and/or hydrolysis of the cyclic carbonates formed.[40–44] In particular, Puglisi and coworkers proposed the reaction mechanism presented in Scheme 3 for PC-BPA.[44] At initial low temperatures

(400–500°C), the authors considered three different reactions: (i) intramolecular exchange reactions that generate cyclic oligomers (Scheme 3a); (ii) hydrolysis reactions that generate phenolic end groups and $CO_2$ (Scheme 3b); and (iii) decarboxylation of carbonate groups that generates ether bridges (Scheme 3c). At higher temperatures (500–700°C), they also proposed three different reactions: (i) dehydrogenation of ether bridges that generate dibenzofuran units (Scheme 3d); (ii) disproportionation reactions of isopropylidene bridges that generate phenyl and isopropenyl end groups (Scheme 3e); and (iii) isomerization of aromatic carbonate functional groups and successive condensation, that generate compounds containing xanthone and fluorenone units (Scheme 3f and g).

In opposition—and contemporary—to the results of Montaudo and co-workers,[40–44] McNeill and Rincon reported that the decomposition of PC-BPA—in the absence of air and moisture, and under continuous evacuation of the volatile products—proceeds mainly by homolysis of the polymer chain and subsequent reactions of the formed radicals, and that ionic ester interchange occurs at low decomposition temperatures and at a slower rate.[40,45,46]

In the last decade, Jang and Wilkie[47] proposed that the main thermal degradation pathways of PC-BPA pyrolysis follow both chain scission of isopropylidene linkages and hydrolysis/alcoholysis reactions as proposed by McNeill and Rincon,[40,45,46] and in less extent the rearrangement of carbonate linkages as proposed by Montaudo and co-workers.[40–44] Scheme 4 presents the degradation mechanism proposed by Jang and Wilkie for PC-BPA.[47] At the beginning of PC-BPA pyrolysis, carbonate groups undergo rearrangement (Scheme 4a), and then decarboxylation or cross-linking reactions occur (through esterification), respectively, generating $CO_2$ and $H_2O$ (Scheme 4b and c). This last reaction generates cross-linked structures that are eventually converted into char. Simultaneously, chain scission of the methyl group of isopropylidene linkage also occurs via a homolytically cleavage, generating phenyl or aliphatic end groups, such as propyl (Scheme 4d), ethyl (Scheme 4e and f), and methyl (Scheme 4g). Regarding carbonate linkage, it could be transformed by (i) hydrolysis reactions that generate two phenol end groups and $CO_2$ (Scheme 4i); (ii) alcoholysis reactions—including phenolysis—that generate small aromatic carbonates, such as diphenyl carbonate (Scheme 4j); and (iii) thermal homolytic cleavage that generates phenol and highly reactive phenyl radicals and $CO_2$ (Scheme 4k). As conversion increases, more alcohol groups are produced, which could act as the source for alcoholysis reactions. The presence of a high content of BPA in several works could imply that hydrolysis/alcoholysis of carbonate linkage is the main pathway for its formation.[30,59–62] As observed in Scheme 4, many reactions
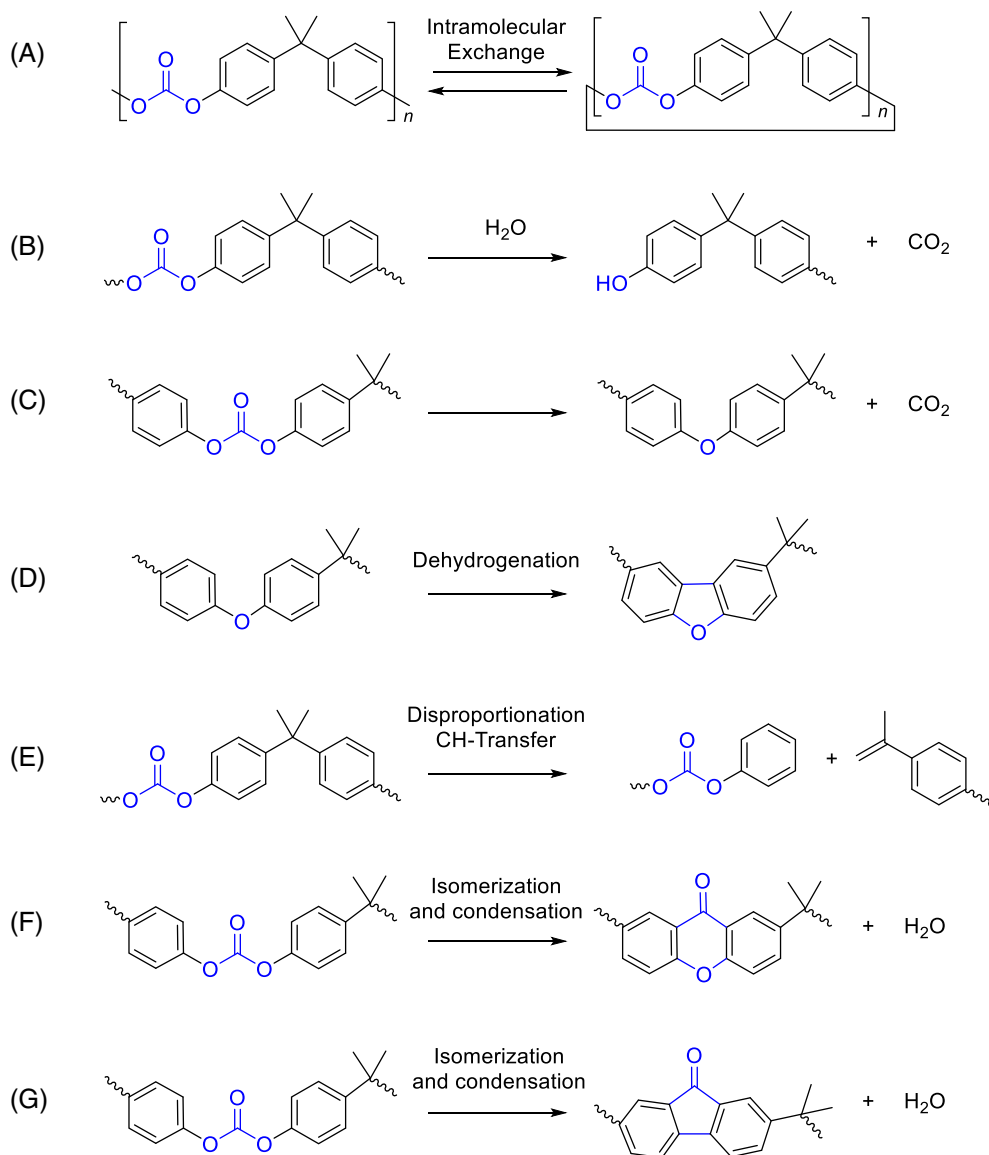
lead to the formation of oligomers that could then act as char precursors. Similarly, Achilias and co-workers[56] suggested a mechanism for the PC-BPA degradation that supports the mechanism in Scheme 4 proposed by Jang and Wilkie.[47]

More recently, several authors have theoretically investigated the degradation of PC-BPA using computational simulations.[48–50] Based on the experimental results and different theoretical models—density functional theory methods,[48,50] molecular dynamics simulation,[49] and reactive molecular dynamics simulation[50]—the authors proposed several possible thermal degradation pathways, which take into account hydrolysis, homolytic cleavage, and rearrangement reactions. It seems that the main degradation pathway depends on the degradation conditions, and that more than one mechanism may occur simultaneously or in overlapping temperature regions. Thus, it is apparent that complex processes are involved in the

thermal degradation of PC-BPA, and that it is still difficult to get insights into the detailed pyrolysis mechanism.

## 2.1.2 | Chemical composition of pyrolysis products

The gas produced during thermal pyrolysis is usually a mixture of $CO_2$, $CO$, $H_2$ and $CH_4$ while the liquid fraction is a wide distribution of aromatics and ether compounds.[30,61] Aromatics such as benzene, toluene, and xylenes can be employed in the petrochemical industry as polymeric precursors, for example, for polyurethanes. Similarly, polyphenols can be employed as precursors in paint and adhesives industries.[62,64]

Table 1 summarizes the articles that have focused on the quantification of the chemical compounds found in the liquid fraction.[30,58–62] The table presents the main
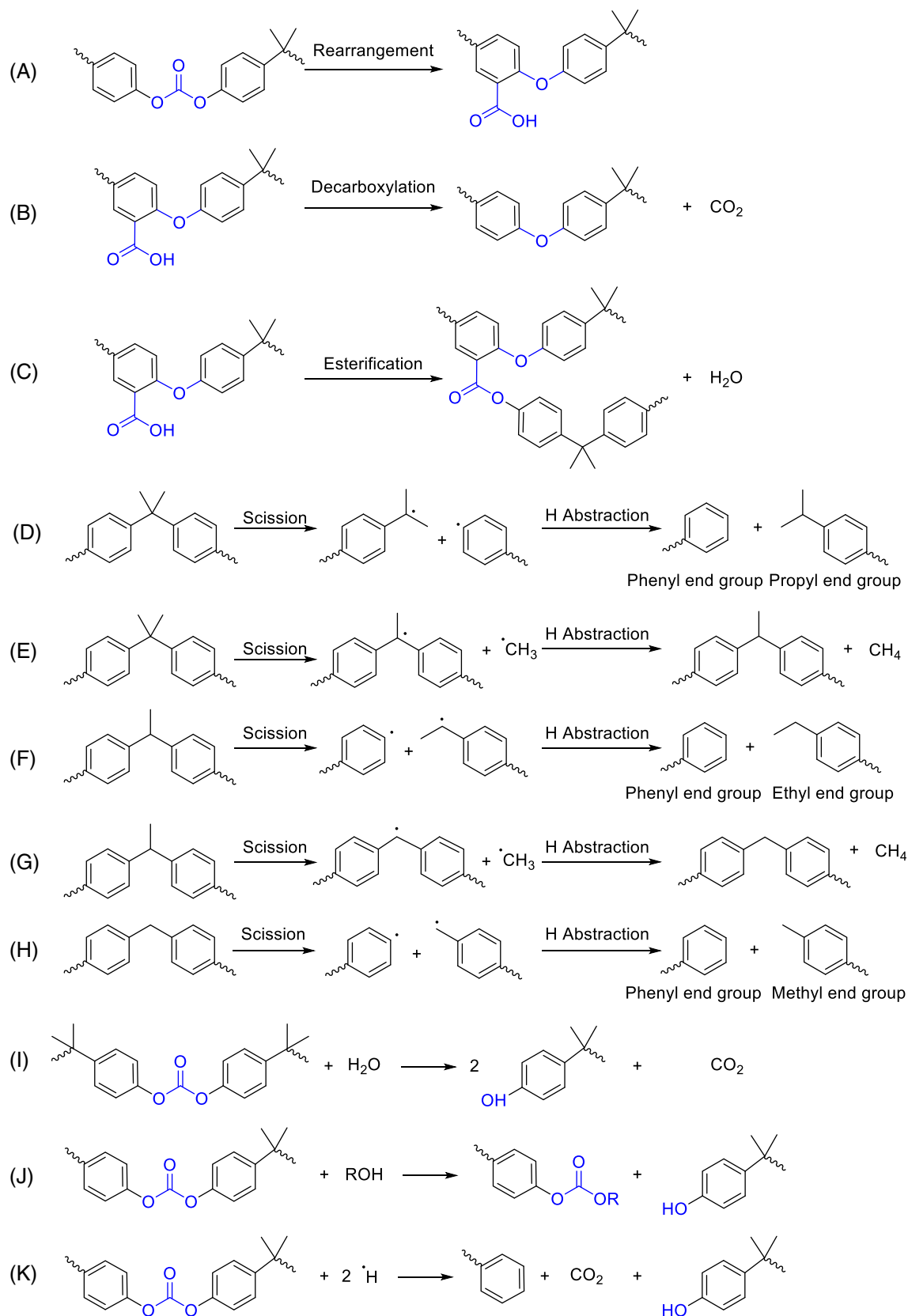
**SCHEME 4** Degradation mechanism during PC-BPA pyrolysis[51]

process parameters, fraction compositions, and major chemical compounds in the liquid oil. As observed, some authors compared commercial PC-BPA with PC-BPA recycled from the electronic industry, such as CDs and DVDs. It also shows that different temperatures and residence times were employed for the thermal pyrolysis of

**TABLE 1** Main articles found in the literature that quantified the chemical compounds present in the liquid fractions of PC-BPA thermal pyrolysis

| Material | PC-BPA | PC-BPA | CD | DVD | PC-BPA | CD | PC-BPA | CD | PC-BPA | PC-BPA |
|---|---|---|---|---|---|---|---|---|---|---|
| *Process parameters* | | | | | | | | | | |
| $T$ (°C) | 400 | 450 | 450 | 450 | 550 | 550 | 600 | 600 | 700 | 900 |
| Time (min) | 60 | 320 | 320 | 320 | 17 | 17 | 15 | 15 | 10[a] | 10[a] |
| *Product fractions* | | | | | | | | | | |
| Gas | > 95 | 16.5 | 13.7 | 15.6 | 6.6 | 8.6 | 18.5 | ~19 | – | – |
| Liquid | 1.2 | 40.2 | 47.1 | 50.8 | 63.0 | 80.4 | 57.0 | ~51 | – | – |
| Solid | < 5 | 43.3 | 39.2 | 33.6 | 30.4 | 11.0 | 24.5 | ~29 | – | – |
| *Main components of liquid fraction* | | | | | | | | | | |
| Phenol | 8.22 | 6.98 | 7.09 | **18.72** | **32.1** | **24.9** | 5.74 | 5.38 | **35.61** | 10.90 |
| Methyl phenol (cresol) | 11.27 | **29.70** | **14.70** | **18.71** | 12.9 | 8.8 | 14.37 | 18.47 | 1.83 | 14.81 |
| Ethyl phenol | 11.22 | 18.07 | 10.31 | 14.49 | 2.8 | 5.3 | 8.17 | 10.42 | 1.12 | 7.71 |
| Propyl/isopropyl phenol | 14.45 | 4.61 | 6.26 | 15.72 | 5.6 | 7.6 | – | – | – | 0.47 |
| BPA | **18.60** | 10.64 | 12.55 | 5.77 | 16.0 | **31.9** | 27.44 | 40.07 | 6.73 | **21.84** |
| Diphenyl carbonate | 13.44 | – | – | – | 0.3 | 0.4 | – | – | **20.19** | 0.45 |
| Reference | 59 | 60 | 60 | 60 | 61 | 61 | 30,62 | 30,62 | 58 | 58 |

*Note:* The highest values for each process are shown in bold.

[a]Time in seconds.

PC-BPA, ranging from 400°C to 900°C and 10 s-340 min, respectively.

The first study was carried out by Sheehan and co-workers, who investigated the pyrolysis of PC-BPA at 700°C and 900°C without separating the gas and liquid fractions at the end of the process.[58] The authors observed that the product yield is much lower at 700°C than the yield obtained at 900°C, but the number of chemical compounds increases from 16 to 25. In a more complex work, Tsai and co-workers used an isothermal reactor under continuous $N_2$ flow at atmospheric pressure and at a reaction temperature of 400°C.[59] Their results showed that under these conditions, almost the totality of PC-BPA decomposed in char residue, and only 1.2% was liquid oil. Employing a similar temperature (450°C) under $N_2$ atmosphere, but in a semibatch glass reactor, Kaji and co-workers carried out the thermal degradation of commercial PC-BPA and PC-BPA recycled from CDs and DVDs.[60] The products obtained consisted of a 14–16 wt% gas fraction, a higher 40–50 wt% liquid fraction, and a 34–43 wt% solid residue. In all cases, over 20 products were quantified in the liquid fraction, consisting mainly of aromatics, phenols, and ethers compounds. The liquid composition of CDs and DVDs were similar to that of commercial PC-BPA, with only slightly different concentrations of each compound. Similarly, the group of Achilias published several articles regarding the pyrolysis of commercial PC-BPA and PC-BPA recycled from CDs.[30,61,62] In a preliminary work, Achilias

and co-workers employed a laboratory-scale fixed bed reactor at 550°C.[61] The reaction system proved to improve the liquid oil fraction to an important 63–80 wt % containing at least 15 chemical compounds, while the gas and solid fractions were reduced to 7–9 wt% and 11–30 wt%, respectively. Later, the group of Achilias employed a fixed bed tubular reactor under inert atmosphere at a slightly higher temperature of 600°C.[30,62] The gaseous fraction consisted of a 15–20 wt%, the liquid fraction on a reasonable 50–60 wt%, and the char residue on a 20–30 wt%. The liquid fraction was a mixture of different aromatics, aliphatics, polyaromatic hydrocarbons, phenols, and ethers, with the phenols representing around 71% and consisting of eight products.

In most cases, the articles in Table 1 reported that the main liquid products were phenol, cresol, and BPA. These chemical compounds can be employed as precursors in the polymer industry. However, the thermal pyrolysis of PC-BPA generates a wide distribution of products, which decrease the selectivity and final yield of the compounds of interest, and requires several appropriate separation and purification operations.

## 2.2 | Thermal-catalytic pyrolysis

The use of catalysts in the pyrolysis of PC has been investigated since the late 1990s.[30,58,59,62,64–66] In general, the aim of employing thermal-catalytic pyrolysis is to

increase the conversion rate at lower temperatures and to reduce the solid fraction while increasing the liquid and gas fractions, and/or increase selectivity to desired chemical compounds at relatively high temperatures.[1,31]

A wide range of catalysts have been employed in the thermal-catalytic pyrolysis of PC-BPA in order to study their effect on the degradation process, including metals,[58] metal chlorides,[59,65] zeolites,[30,62] basic oxides,[30,62] and mesoporous materials.[62,64,66] In a pioneering study, Sheehan and co-workers reported that the presence of 5 wt% copper increases the conversion and yield of several pyrolysis products, especially at a temperature of 900°C.[58]

Regarding metal chlorides employed as active catalysts, Blazsó investigated the effect of a 20–40 wt% of copper and iron chlorides ($FeCl_2$, $FeCl_3$, $CuCl$, and $CuCl_2$) on the pyrolysis of PC-BPA at 600°C.[65] The use of these catalysts generates a higher amount of phenol and BPA, and increases the number of minor products, thus widening the product distribution. Similarly, Tsai and co-workers employed a 10 wt% of different metal chlorides ($NaCl$, $MgCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 6H_2O$, $ZnCl_2$, $AlCl_3 \cdot 6H_2O$, and $SnCl_2 \cdot 2H_2O$) in the thermal-catalytic pyrolysis of PC-BPA at a lower temperature (400°C).[59] The authors observed that only four of these catalysts ($SnCl_2$, $ZnCl_2$, $FeCl_3$, and $MgCl_2$) enhanced PC-BPA degradation and increased conversion from 8.5% in thermal pyrolysis to more than 70% in thermal-catalytic pyrolysis, thus generating more gas and liquid fractions and less char residue. In these four cases, the gas fraction was approximately 15–20 wt% and the liquid fraction a high 50–70 wt%. In particular, the choice of $SnCl_2$ and $ZnCl_2$ exhibited substantial effects, such as lowering the weight loss onset temperature and the effective degradation temperature to 325–350°C, increasing the conversion, and narrowing the product distribution in the liquid fraction from 20 compounds in thermal pyrolysis to 8–10 in thermal-catalytic pyrolysis. As in thermal pyrolysis, two of the main liquid compounds are phenol and PBA, together with isopropylphenol, diphenyl ether, and diphenyl carbonate.

Regarding catalysts with different acid/basic behavior, the group of Achilias carried out a series of investigations.[30,62] In the first work, this group studied the effect of nine catalysts in the product composition of commercial PC-BPA pyrolysis, including acid zeolites (two different ZSM-5, silicalite, and a ultrastable Y faujasite CBV 712), acid mesoporous materials (MCM-41 alumino-silicate, and γ-$Al_2O_3$), and basic oxides (two different MgO, and CaO).[62] Almost all catalysts promoted the generation of phenol compounds in the liquid fraction, with the highest production observed in the presence of the CaO and MgO basic oxides. Basic catalysts even favor PC-BPA degradation at lower temperatures compared to both thermal and acid thermal-catalytic pyrolysis. However, most of these catalysts seem to promote the formation of specific single ring compounds at the expense of the production of BPA. In a parallel work, the group of Achilias only studied the effect of MgO and ZSM-5 zeolite in the pyrolysis of commercial and recycled PC-BPA.[30] The results agree with their previous article, indicating an extended degradation of PC-BPA in the presence of both catalysts.[62] In addition to the articles reported in Table 1, Ragauskas and co-workers focused their research on converting PC-BPA into monocyclic aromatics by employing three different Fe—Ce/$Al_2O_3$ catalysts prepared by different methods.[64] The results indicated that Fe—Ce/$Al_2O_3$ prepared by coprecipitation possessed superior catalytic activity due to its high content of weak acid sites, large pore volume, high surface area, and well dispersion of Fe and Ce active species, leading to an approximately three-fold increase in specific monocyclic aromatic hydrocarbons compared to the thermal pyrolysis. More recently, with the aim of mitigating toxic pollutants and generating more value-added syngas ($CO + H_2$), Kwon and co-workers studied the effect of Ni/$SiO_2$ and Co/$SiO_2$ catalysts in the pyrolysis of PC-BPA recycled from automotive headlight housing (AHH), by employing $CO_2$ as reactive gas.[66] The authors observed that gas phase reactions involve $CO_2$ and BPA and its derivatives, enhancing the syngas formation. In addition, the presence of catalysts increased the syngas formation more than one order of magnitude regarding the thermal pyrolysis of PC-BPA.

As it has been previously discussed, specific chemical compounds could be obtained by selecting a suitable catalyst, but further work should be done in order to make thermal-catalytic pyrolysis an environmental-friendly chemical process for PC recycling, especially when the final objective is the production of chemical or polymeric precursors.
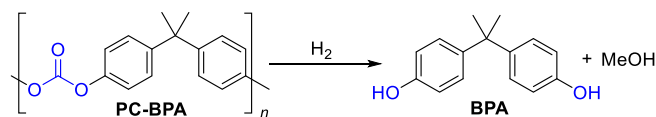
# 3 | DEPOLYMERIZATION BY HYDROGENATION REACTIONS

As indicated earlier, thermal and thermal-catalytic pyrolytic processes afford complex reaction mixtures whose compositions strongly depend on the experimental conditions and the nature of the catalyst employed for the depolymerization reactions. Therefore, additional time and energy consuming purification steps would be needed for the isolation of any particular chemical of interest. In clear contrast, hydrogenative depolymerization of PC-BPA affords much simpler reaction mixtures from which BPA and methanol (MeOH) could easily be recovered. In fact, over the last 10 years catalytic hydrogenation has evolved to a promising tool for the clean
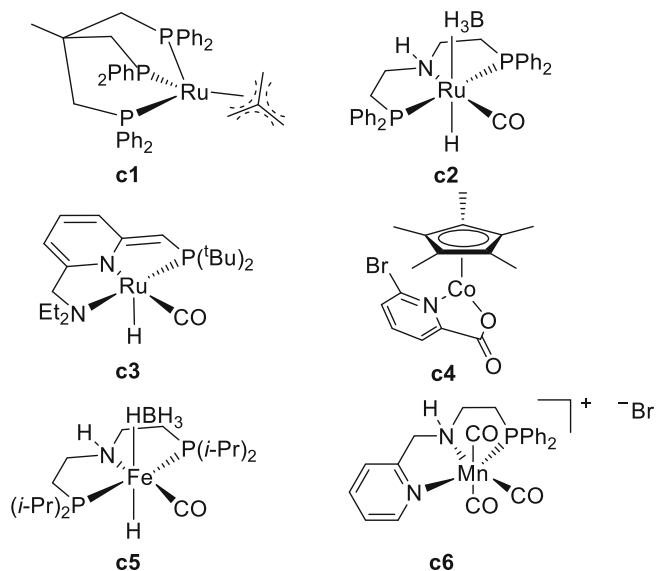
recycling of various plastics, including polyesthers, polyurethanes and PCs (Scheme 5).[67–69]

Although initial works suggested that Ru complexes appeared to be particularly well suited for PC-BPA hydrogenation, recent efforts have been made in order to extent the scope of the process using Fe, Mn and Co complexes as much more affordable and benign catalytic systems. The results obtained so far seem to suggest that Pincer-like structures are privileged ligands for this family of catalytic hydrogenations (Scheme 6).

In the recent study, molecular Ru catalyst **c1** (1 mol %) yielded almost quantitative conversion and selectivity in the hydrogenation reaction of PC-BPA ($H_2$ [100 bar], dioxane 140°C, 16 h) of PC-BPA (Scheme 6). For the success of the process, bis(trifluoromethanesulfonyl) imide as co-catalyst was also required to activate the complex.[70] Complex **c1** showed excellent performance in the hydrogenation of PC-BPA wastes, like standard drinking cups and CDs. The catalytic system proved to be insensitive to the impurities of such composite materials, affording in both cases quantitative depolymerization yields using a low catalyst load (0.33 mol%).[70] In connection with this work, Ru-MACHO complex **c2** also proved to be effective for the hydrogenation of PC-BPA, producing BPA yields of up to 99% ($H_2$, [45 bar], THF, 140°C).[71]

Milstein catalyst **c3** was also found to be efficient for the same hydrogenation.[72]

The catalytic cycle depicted in Scheme 7 has been proposed for the hydrogenation of carbonates. In these reactions **c7** is converted into catalytically active species **c7a** by base reaction to eliminate HCl. **c7a** is then reduced (via transition state **c7a***) by molecular hydrogen to yield hydride **c7b**, which reacts with the carbonate affording an alcohol and regenerating active **c7a** (via transition state **c7b***). It seems likely that the **c2**-catalyzed hydrogenative depolymerization of PC-BPA operates under a similar mechanism.

PC-BPA hydrogenations with catalyst **3c** probably proceed by a closely related mechanism to that presented in Scheme 7. The original mechanism proposed by Milstein for the hydrogenation of cyclic carbonates with **3c** is presented in Scheme 8.[73]

With the aim of imitating the performance of a tridentate Ru Pincer ligand, Enthaler and co-workers recently designed a simple approach by which and in situ formed Ru complex efficiently catalyze the hydrogenation of PC-BPA.[74] The catalytic complex is composed by [RuClH(CO)(PPh₃)₃]/H₂NCH₂CH₂-P-(iPr)₂ couple, which



**SCHEME 5** Depolymerization of PC-BPA by hydrogenation reaction



**SCHEME 6** Major catalysts employed for depolymerization of PC-BPA by hydrogenation reactions.
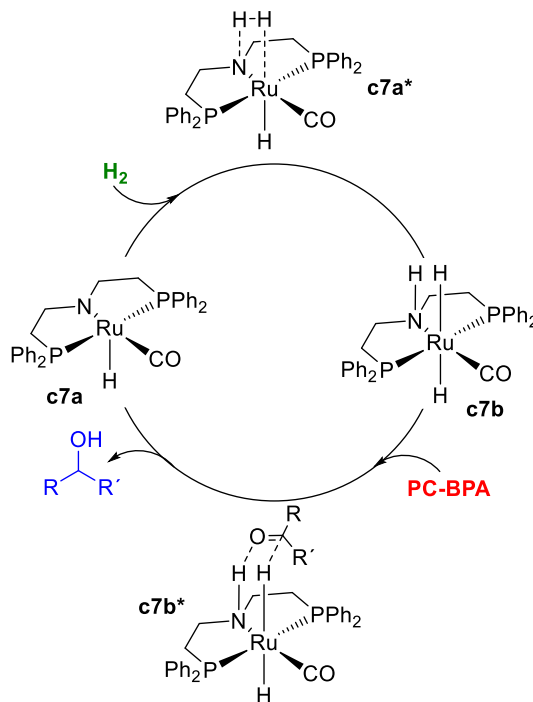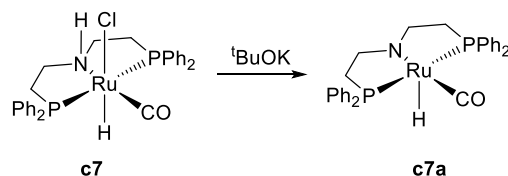


**SCHEME 7** Proposed mechanism for the catalytic hydrogenation of PC-BPA using **c7** catalyst

**SCHEME 8** Proposed mechanism of hydrogenation with Milstein **3c** catalyst[73]
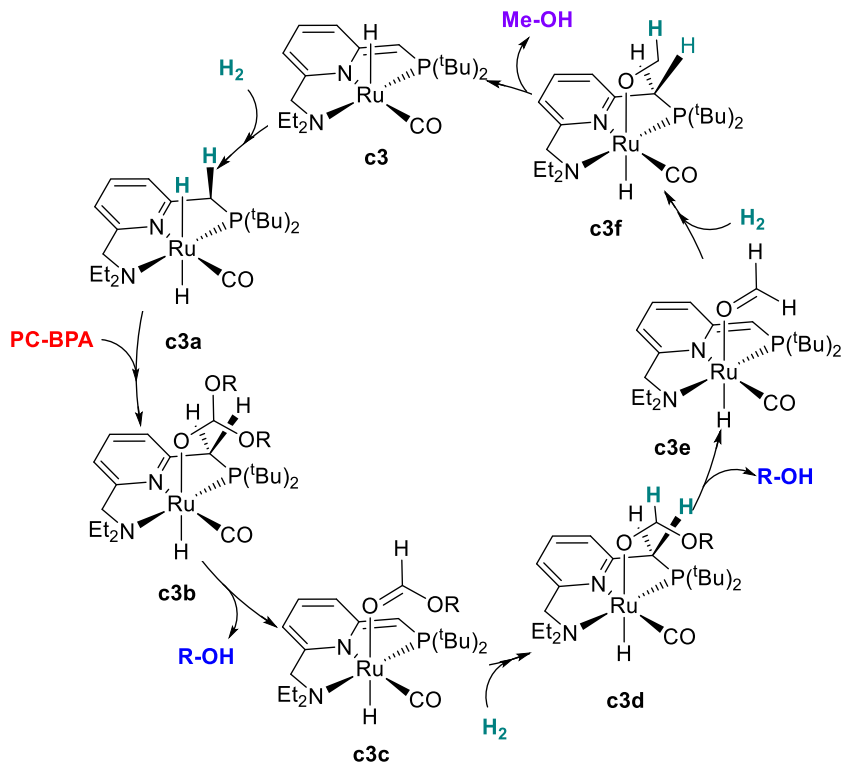


also proved to be successful for the depolymerization of PC-BPA wastes, such as DVDs and safety goggle samples.

High valence Co complex **c4** has successfully been employed for the catalytic hydrogenation of carbonates and PC-BPA (Scheme 6).[75] Thus, hydrogenolysis (60 bar of $H_2$) of PC-BPA and even pieces of a PC-BPA DVD, at 160°C for 24 h in dibutyl ether afforded BPA with yields of 83 and 66% respectively. These reactions required loads of KO$t$-Bu as high as 40 mol% to yield good conversions. Although in this work a mechanism is not provided, a mechanism related to that explored by the group of Beller for the hydrogenation of $CO_2$ may be involved.[76]

Fe Pincer complex **c5** has been employed by the group of Enthaler for hydrogenation/depolymerization of PC-BPA (Scheme 6).[77] The optimized reaction conditions required 2 mol% of the catalyst and a pressure of 45 bar of $H_2$ at 120°C in THF for 24 h. The catalytic system proved to be successful for the depolymerization of PC-BPA composite materials such as a ball-milled DVD and safety goggles, producing excellent depolymerization yields.[77] It is worth to mention that the process does not need any base or any other additive. PC-BPA was mixed with various polymers, including PET, PLA and PCL, among others, and the selective hydrogenation of PC-BPA was studied under the optimized experimental conditions. In these cases, selective hydrogenation of PC-BPA was achieved. For PC-BPA/PLA mixture, the reduction of the molar mass of PLA was detected by DOSY-NMR.[77]

In connection with this work, Werner recently used Fe Pincer catalyst **c8** and KO$t$-Bu as base for an efficient transfer hydrogenation of cyclic carbonates using isopropyl alcohol as hydrogen donor and THF as solvent. The catalytic system probed to be promising for the hydrogenation of poly(propylene carbonate), yielding 65% and 43% of propylene glycol and MeOH under a set of optimized experimental conditions.[78] The function of the base is to convert complex **c8** into the catalytically active species **c8a**, which upon reaction with $i$-PrOH gives **c8b**, which is the actual hydrogenation reagent (Scheme 9).

The similarity of **c5** and **c8** and the resemblance of **c8b** with **c3a** and **c7b** could suggest the operation of related mechanism.

The group of Rueping conceived Mn catalyst **c6**, which was shown to be efficient for the hydrogenation of various carbonates (Scheme 6).[79] In these reactions, catalyst and base (KO$t$-Bu) loads of 1 and 2.5 mol% respectively were employed under $H_2$ pressure of 50 bar. This interesting system has not so far been evaluated for the depolymerization of PC-BPA. For these reactions a catalytic mechanism closely related to that presented in Scheme 8 was proposed.

An interesting organocatalytic hydrosilylation/depolymerization of PC-BPA was published by Cantat and co-workers a few years ago.[80] In their work, the reaction of PC-BPA with $Et_3Si$-H in the presence of 2 mol% of tris(pentafluorophenyl)borane $(B[C_6F_5]_3)$ afforded a mixture of silylated BPA (82%) and methylated product **q2** (28%), which is probably formed by a Friedel-Craft
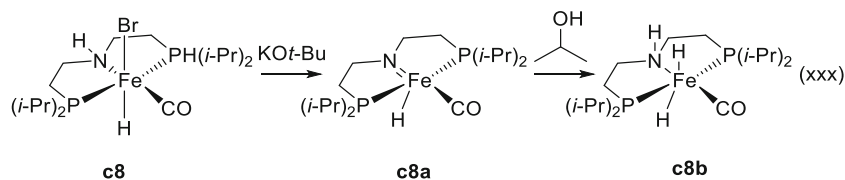
**SCHEME 9**  Activation of **c8** catalyst
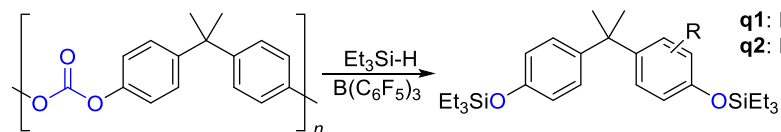


**SCHEME 10**  Organocatalytic hydrosilylation/depolymerization of PC-BPA[80]

alkylation reaction, where an electrophilic methyl derivative should be formed upon reaction of the carbonate moiety of the PC-BPA polymer (Scheme 10).

Tetramethyldisiloxane ($Me_2SiHOSiHMe_2$, TMDS) performed outstandingly in this reaction, yielding exclusively the silylated BPA reduction product (98%). In contrast, the trityl salt of $B(C_6F_5)_3$ [$Ph_3C^{+-}$ $B(C_6F_5)_3$] yielded a mixture of **q1** and **q2** in 47 and 26%, respectively. The scope of this reductive depolymerization has also been studied using an Ir complex as cationic catalyst. The reactions of PC-BPA with $Et_3Si$-H afforded **q1** exclusively, which was ultimately converted to BPA by reaction with tetrabutyl ammonium fluoride hydrate. Under similar reaction conditions PC-BPA provided a gel, which reacted with $NaOH/CH_3OH$ to give clean BPA.[81]

## 4 | DEPOLYMERIZATION BY HYDROLYSIS REACTIONS

### 4.1 | Hydrolysis of PC-BPA in water

Hydrolysis of PC-BPA is a simple, economical, and environmentally friendly chemical recycling method that allows the recovery of the BPA monomer for reuse. The drawback of this methodology is that PC-BPA is a rigid and hydrophobic polymer, so the hydrolysis reaction in water is a heterogeneous solid–liquid system. Therefore, it is necessary to use high temperatures and pressures that swell or melt the PC-BPA, decrease the viscosity and polarity of water and increase its diffusivity, in order to favor contact between the reagents. As consequence of the hard conditions required, BPA, the primary product of the PC-BPA hydrolysis, is further degraded to phenol or *p*-isopropenyl phenol (IPP) (Scheme 11).[82] This leads to a loss in selectivity and, consequently, to a decrease in the usefulness of the reaction.

In this regard, Chiba and co-workers studied the hydrolytic depolymerization of PC-BPA in sub-critical and super-critical water.[83] No thermal decomposition

was observed when the reaction was conducted below 230°C for 24 h. Moreover, a 31.8% products mixture was obtained when the hydrolysis was performed at 250°C for 10 h. An appreciable yield (89%) was only obtained when the reaction was carried out at 430°C for 1 h. Under these conditions, no selectivity was observed, since BPA was further degraded to phenol or IPP.[82] Furthermore, the addition of NaCl, which affects the density of water, did not promote hydrolysis even at 300°C, and only a slight improvement was observed when $CH_3COOH$ was added as a proton donor source. On the other hand, the addition of $Na_2CO_3$ alkaline salts promoted the PC-BPA decomposition reaction. Phenol was selectively formed when 0.4 wt% $Na_2CO_3$ was used, and the reaction was carried out at a temperature above 240°C.[83]

Burruss and co-workers also observed that in subcritical $H_2O$, at short reaction times, PC-BPA is stable at temperatures below 265°C.[84] This group showed, using a fused silica capillary reactor, which below this temperature there were physical changes in PC-BPA (swelled at 100°C and melted at 200°C). Complete PC-BPA decomposition was observed when the reaction was carried out at 280°C and approximately 6.4 MPa for 46 min.[84] On the other hand, it was shown that manganese acetate (Mn[Ac]$_2$) accelerates the dissolution and thus the formation of a homogeneous solution of PC-BPA in hot compressed water, and catalyzes the depolymerization of PC-BPA. When the reaction was performed at 280°C for 20 min with 2.0% of Mn(Ac)$_2$, yields of BPA and phenol of 55.25% and 18.63% were respectively achieved.[85]

Water is an accessible, non-toxic, and inexpensive solvent, making it ideal for plastic depolymerization reactions. Separation of the reaction products involves the use of an organic solvent or the spending of energy in water evaporation. Therefore, it is preferable to minimize the amount of water used. With this aim, Hironaka and co-workers investigated the hydrothermal hydrolysis of PC-BPA in high-pressure high-temperature water (HHW) and high-pressure high-temperature steam (HHS).[86] Both reactions were carried out at 300°C, with about 480 mol
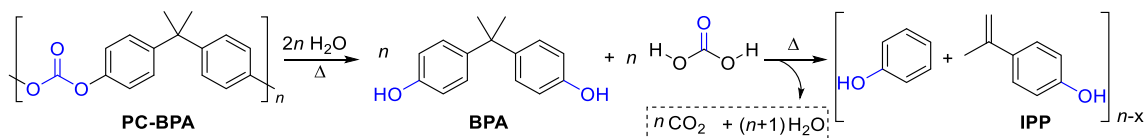
**SCHEME 11**  PC-BPA hydrolysis and BPA degradation at high temperature[82]

$H_2O$ per mol of carbonyl group for HHW (water pressure 12.2 MPa) and about 16 mol $H_2O$ per mol of carbonyl group for HHS (water pressure 7.9 MPa). Under these reaction conditions, although $H_2O$ equivalents are higher in HHW than in HHS; the decomposition of PC-BPA was faster (5 min vs. 300 min) and more selective (80% vs. 50% BPA yield) in HHS than in HHW. The researchers suggest that the different decomposition rates could be due different mechanisms. In HHW depolymerization the reaction probably occurs by bulk erosion, whereas surface and bulk erosion may occur competitively in HHS. This could be related to the high diffusivity and reactivity of $H_2O$ in HHS. For a clear explanation of the possible mechanism see reference. Furthermore, it was shown that in steam atmosphere magnesium and calcium oxides and hydroxides (MgO, $Mg(OH)_2$, CaO, and $Ca(OH))_2$ catalyze the depolymerization by hydrolysis of PC-BPA.[87–89]

As mentioned above, PC-BPA is a rigid and insoluble polymer, its hydrolysis in pure water as solvent requires harsh conditions. This leads to BPA decomposition into phenol and IPP (Schemes 11 and 12).[90] Therefore, if the intention is to perform depolymerization by hydrolysis to obtain the starting monomer (BPA), the reaction must be performed at lower temperatures. To this end, additives that promote the reaction (catalysts) and/or solvents that homogenize the PC-BPA and the water are necessary (Scheme 12). The additives used generally seek to activate: the carbonyl group (e.g., Lewis acids); the nucleophile (bases, bulky counterions, and hydrogen bridge-bond acceptors); or both. Because of the chemical similarity, the additives that were explored to favor the hydrolysis of the carbonate group of PC-BPA were those that promote the hydrolysis of esters. For clarity of reading, they were grouped into: bases and protic acids (using organic solvents or phase transfer catalysts), ionic liquids and metal.

## 4.2 | Hydrolysis of PC-BPA promoted by bases or Protic acids in organic solvents

In this sense, $CH_3CO_2H$, $H_2SO_4$, HCl and $HNO_3$ were used as proton donor additives ($m_{additive}$:$m_{PC-BPA}$ = 4) in the hydrolysis of PC-BPA at 250°C for 1 h, but no

polymer decomposition was observed.[90] Furthermore, under this experimental conditions, ethanol, calcium carbonate and sodium chloride showed no activity. Decomposition was not observed even at 300°C when the reaction was carried out in toluene or benzene as solvent. Unlike acidic additives, the addition of alkaline compounds did promote the decomposition reaction of PC. When $CO(NH_2)_2$ or $NH_4OH$ (4 wt%) were used as additives, the yields of BPA were close to 40%. The use of $Na_2CO_3$ showed higher selectivity for phenol formation, achieving a yield of 47 wt%. Moreover, the yield of phenol reached 65.0 wt% (IPP 3 wt%) when the reaction was carried out in a 100 mM $Na_2CO_3$ aqueous solution at 250°C for 1 h. The decomposition reaction was shown to be accelerated by an increase in $Na_2CO_3$ concentration. Thus, higher base concentrations allow the reaction to be carried out at a lower temperature. Therefore, when the hydrolysis reaction was carried out in a 1000 mM $Na_2CO_3$ aqueous solution at 130°C for 3 h, complete decomposition of polymer was observed, and a 56 wt% of BPA was obtained as the main product.[90]

Ge and co-workers reported that the use of organic solvents and NaOH promotes the hydrolysis of PC-BPA under mild conditions.[91] Hydrolytic decomposition of the polymer was not observed when the reaction was conducted with NaOH as a catalyst without co-solvents. However, the yield of BPA was close to 70% when the reaction was carried out with NaOH as catalyst in dioxane, DMF, THF, or N-methyl-2-pyrrolidone at 65°C for 8 h. In these systems, it was found that under the optimal reaction conditions: 100°C, $H_2O$ (10 equiv, $m_{PC-BPA}$: $m_{H2O}$ = 1:0.7), NaOH (63 mol%, $m_{PC}$:$m_{NaOH}$ = 10:1), time 8 h in dioxane ($m_{Solv}$:$m_{PC}$ = 4) as a solvent, the hydrolysis conversion of PC-BPA was almost 100% and the yield of BPA was 94%.[91]

On the other hand, Rahmat and co-workers reported that BPA could be obtained with a 94% yield in only 12.5 min when the previous protocol was carried out at 110°C under microwave heating.[92]

Interestingly, under basic conditions and microwave heating, depolymerization by hydrolysis can be promoted using a phase-transfer catalyst instead of an organic solvent. It was observed that 82% of PC-BPA decomposition could be achieved when the polymer was microwaved at 160°C for 10 min in a NaOH solution (10 w/v%, 3 equiv.)
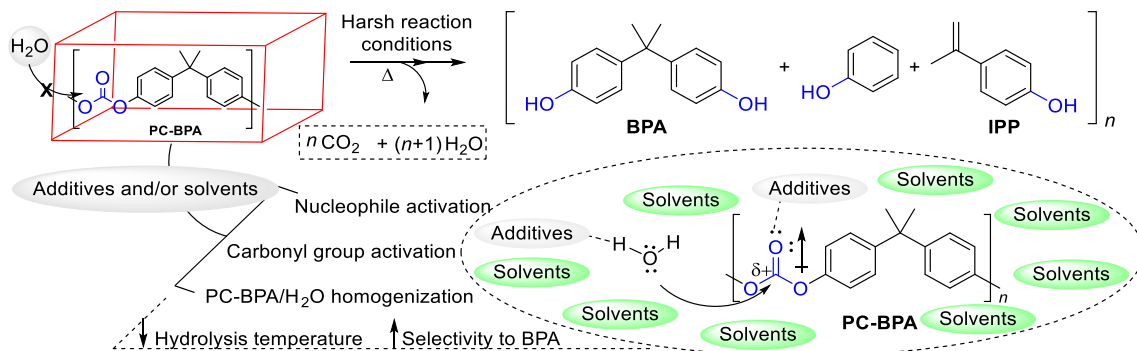
**SCHEME 12**  Reactions condition in PC-BPA hydrolysis

in the presence of 1-hexadecyl trimethyl ammonium bromide (0.001 mol/mol PC-BPA). Under these conditions, the main decomposition product appears to be BPA, but its yield was not reported.[93] To further understand the reaction mechanism, the researchers analyzed the PC-BPA residues and the recovered BPA. They found that no oligomer formation was detected, and the average molecular weight of PC-BPA decreased only slightly. Owing to this, coupled with the fact that the reaction is promoted at temperatures near glass transition points of PC-BPA and to the fact that the PC-BPA has a lipophilic part, which could be inserted into the polymer, the researchers propose that the reaction occurs at the polymer-solution interface. In this way, the cationic part of the catalyst, located on the surface of the polymer, promotes the approach of the nucleophile to the interface, facilitating nucleophilic attack and depolymerization (Scheme 13).[94]

In line with the use of base and organic solvents to smooth the reaction conditions, Nikje and Askarzadeh developed a method that uses NaOH and glycerol/$H_2O$. The yield of BPA was 100% when the decomposition reaction was carried out at reflux for 5.5 h in presence of NaOH (4% based on PC-BPA) in a 30 wt% aqueous glycerol solution.[95] Moreover, water appears not to be necessary when the reaction is conducted in ethylene glycol (**b1**) as solvent under microwave heating at 180°C for 5 min, given that the BPA yield was 92%.[96]

However, this result disagreed with those reported by Frediani and co-workers, who observed that the depolymerization of PC-BPA, in the presence of additives such as (NaOH, $Na_2CO_3$, KOH, p-TsOH, ZnO, $Al_2O_3$, and CaO), in ethylene glycol as solvent produces BPA, its decomposition products and hydroxyethyl ethers of BPA.[97] Moreover, a BPA yield of about 80% was achieved when the reactions were carried out in THF instead of ethylene glycol, with the addition of 3 equiv. of water, under microwave heating at 67°C for 10 min.[97] In contrast to the Frediani protocol,[97] in the system studied by Nijke,[95,96] the carbonate/cyclocarbonate generated by the

reaction of the 1,2-diol with the carbonyl group of PC-BPA, does not react with the BPA anion released in the hydrolysis. This could be due to the system not reaching the proper temperature (180°C vs. 200°C), the carbonate/cyclocarbonate not forming (Nijke did not analyzed the reaction mixture) or decomposing before reacting.

## 4.3 | Hydrolysis of PC-BPA promoted by ionic liquids

Other additives that have shown activity in promoting the hydrolysis of PC-BPA were ionic liquids (ILs). They can be used both to promote the dissolution or swelling of the PC-BPA and as catalysts for the hydrolysis reaction (Table 2). The use of 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) ($m_{IL}$:$m_{PC-BPA}$ = 1.5:1), in the presence of water ($m_{H2O}$:$m_{PC-BPA}$ = 0.35:1) resulted in a 96% yield of BPA when the mixture was heated at 140°C for 3 h (Table 2, entries 1 and 2).[98] When the chloride counterion was used instead of the acetate, a low catalytic activity was observed and the depolymerization had to be performed at a higher temperature (165°C) to achieve good yields (Table 2, entry 4).[99] One advantage of this protocol is that BPA can be recovered by solvent extraction and the IL can be reused without apparently losing its catalytic activity. This higher catalytic activity of [Bmim][Ac] may be due to the fact that it promotes a better dissolution and/or swelling of the polymer, due to the greater similarity between the acetate group and the carbonate group, and its higher basicity (pH = 9.57 vs. pH = 7.56 for [Bmim][Cl]). This basicity may confer a higher coordination capacity to the acetate anion, facilitating the deprotonation of the nucleophile, and promoting the nucleophilic substitution reaction.

The nature of the cationic portion of the IL has also a great influence on its catalytic activity. Therefore, almost 100% PC-BPA conversion and BPA yields above 90% were obtained when the reactions were carried out at 140°C
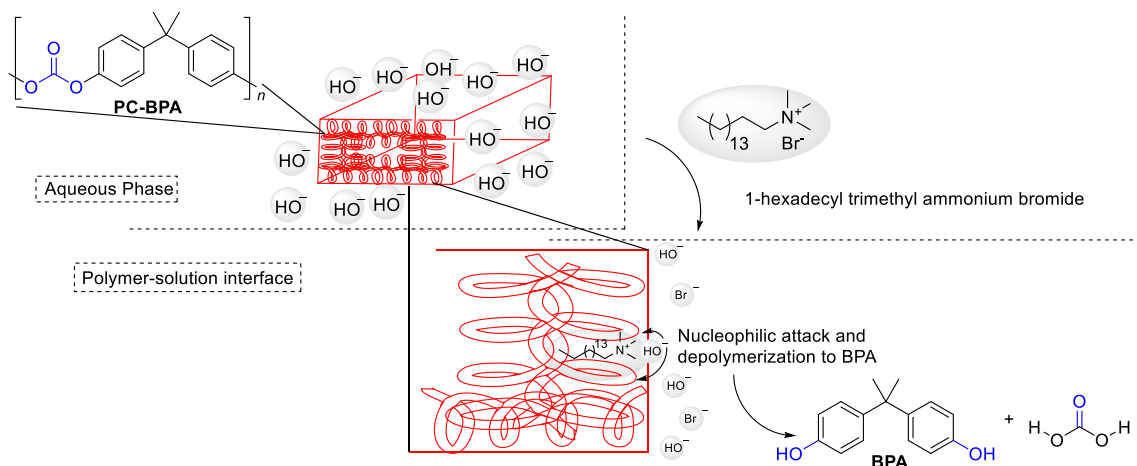
**SCHEME 13**    Proposed mechanism for the hydrolysis of PC-BPA mediated by a lipophilic quaternary ammonium salt.

**TABLE 2**    ILs based catalysts for hydrolysis of PC-BPA

| Entry | Catalyst | $T$ (°C) | Time (h) | IL (mol %)[a] | $n_{H2O}/n_{PC\text{-}BPA}$[b] | PC-BPA conversion (%) | BPA yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | [Bmim][Ac] | 140 | 3 | 25 | 5 | 88.3 | nd | 98 |
| 2 | [Bmim][Ac] | 140 | 3 | 190 | 5 | 100 | 96.2 | 98 |
| 3[c] | [Bmim][Cl] | 175 | 2 | 15 | 139 | 85.3 | nd | 99 |
| 4 | [Bmim][Cl] | 165 | 3 | 215 | 139 | 100 | 95.5 | 99 |
| 5 | [HDBU][LAc] | 140 | 3 | 10 | 42 | 100 | 97 | 100 |
| 6 | [HDBU][Ac] | 140 | 3 | 12 | 42 | 96.7 | 90.5 | 100 |
| 7 | [HDBU][PAc] | 140 | 3 | 11 | 42 | 98.8 | 93.8 | 100 |

[a]Based on the repeating unit of the PC-BPA.
[b]Water/PC-BPA molar ratio.
[c]THF/PC-BPA weight ratio of 1 was used; nd = not determined.

for 3 h, using only a 0.1 wt% of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU)-based ILs (DBU/acetic acid, propionic acid, or lactic acid; [HDBU][OAc], [HDBU][PAc] and [HDBU][LAc]) (Table 2, entries 5–7).[100] This increased catalytic activity can be interpreted in terms of the higher basicity, the ability to dissolve or swell the PC-BPA, and the ability to coordinate the oxygen of the carbonyl group possessed by the amidine group. This way, ILs would facilitate the deprotonation of the nucleophile, the contact between the carbonate group and the nucleophile, and the activation of the carbonate group by electrostatic interaction, furthering the depolymerization reaction (Scheme 14).[100]

## 4.4 | Hydrolysis of PC-BPA promoted by metals

Unlike proton donor acids, Lewis acids from rare-earth metal triflates such as $M(O_3SCF_3)_3$ (M = Sc, Yb, La) promoted hydrolytic depolymerization of PC-BPA. When the reactions were carried out at 160°C for 6 h, PC-BPA conversion were 100% with the three salts. Both scandium and ytterbium triflate were more active than the corresponding lanthanum salt, but the latter was more selective toward BPA formation (97% vs. 14%, and 68%, respectively) (Table 3, entries 1–3). One of the advantages of the system is that lanthanum triflate can be recovered and reused, but as a disadvantage, the method requires the use of an organic solvent (THF), and the depolymerization is not observed when more accessible lanthanum sources ($LaCl_3$, $La_2O_3$ and $La[NO_3]_3.6H_2O$) are used (Table 3, entries 4–6).[101] On the other hand, lower activity (90%) and selectivity (50%) were obtained when trifluoromethanesulfonic acid ($CF_3SO_3H$, triflic acid) was used as an additive (Table 3, entry 7). This indicates that $M(O_3SCF_3)_3$ has a different catalytic behavior than proton donor acids. Because of this, and considering the oxophilic nature of rare earth triflate salts, it was proposed that $M^{+3}$ acts by coordinating the oxygen of the carbonyl group and thereby increasing the electropositive character of the carbonyl carbon atom, activating it to the attack of nucleophiles (Scheme 15).[102]

Funazukuri and co-workers evaluated the catalytic properties of different metal oxides ($MnO_2$, $ZrO_2$, $Al_2O_3$, $CeO_2$, and boron nitride), and diamond powder at 200°C for 5 h, using a weight ratio of 0.15 ($m_{additive}/m_{PC\text{-}BPA}$) for additives and 31 for water ($m_{H2O}/m_{PC\text{-}BPA}$).[103] Under these reaction conditions only $CeO_2$ had an appreciable catalytic activity, achieving complete PC-BPA depolymerization and generating BPA in a yield near to 70% (Table 3, entry 8). As expected, higher catalytic activity was observed when $CeO_2$ nanoparticles were used instead of commercial $CeO_2$. The use of the additive at a weight ratio of only 0.03 achieved a 90% yield of BPA at 180°C, temperature at which commercial $CeO_2$ was not active (Table 3, entries 8 and 9). This temperature difference would indicate that the different catalytic capabilities of the two forms of $CeO_2$ cannot be attributed solely to their different crystal (particle) size. It is to be expected that the morphology of the nanoparticle plays an important role.[104]
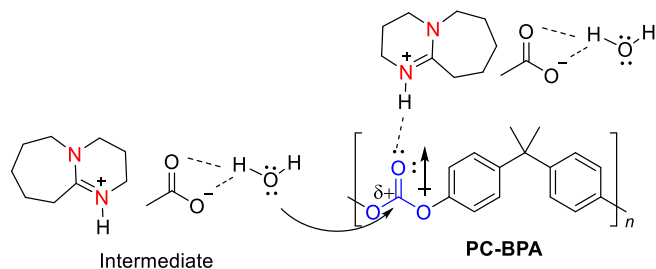


**SCHEME 14**    Possible action of ILs in the hydrolysis of PC-BPA[100]

In an interesting approach, Nacci and co-workers evaluated the synergy in the catalytic activity of a dual system capable of acting as a Lewis acid (ZnO nanoparticles) and a base (counteranions of quaternary ammonium salts or ILs).[105] Although the protocol was investigated and optimized for alcoholysis and aminolysis, when applied to the hydrolytic depolymerization of PC-BPA, BPA was obtained in a yield higher than 95% when the reaction was carried out at 100°C for 7 h using 5 mol% of ZnO nanoparticles (NPs) and $NBu_4Cl$ as additives, and THF as solvent (Table 3, entry 10). Under these conditions, the additives mixture showed better catalytic activity than that obtained with the use of the additives separately. Moreover, ZnO-NPs can be recovered and reused with a slight loss of activity.[105]

Later, Schingaro and co-workers studied the hydrolytic depolymerization of PC-BPA using chlorite, a natural clay mineral.[106] The study showed that chlorite (70 wt % vs. PC-BPA) promoted quantitative hydrolysis of PC-BPA when the reaction was carried out at 200°C for 6 h using a $H_2O$/PC-BPA weight ratio close to 1 ($n_{H2O}/n_{CO3}$ close to 14; or 7 equiv. of $H_2O$ for each C—O bond to be cleaved) in THF as organic solvent. Under this reaction condition, BPA was obtained selectively with a yield of 98% (Table 3, entry 11). However, the catalytic activity of chlorite clearly decreased when it was reused in subsequent cycles.[106]

Although heterogeneous catalysts and ILs are promising alternatives for smoothing hydrolysis conditions, more research will be needed to establish economically

**TABLE 3**    Earth metal triflates and metal oxides catalysts for hydrolysis of PC-BPA

| Entry | Catalyst | $T$ (°C) | Time (h) | $m_{Cat}/m_{PC\text{-}BPA}$[a] | $n_{H2O}/n_{PC\text{-}BPA}$[b] | $m_{THF}/m_{PC\text{-}BPA}$[c] | PC conversion (%) | BPA yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | La(O$_3$SCF$_3$)$_3$ | 160 | 6 | 23.3 | 13.9 | 10 | 100 | 97 | 101 |
| 2 | Sc(O$_3$SCF$_3$)$_3$ | 160 | 6 | 19.7 | 13.8 | 10 | 100 | 14 | 101 |
| 3 | Yb(O$_3$SCF$_3$)$_3$ | 160 | 6 | 24.5 | 14.2 | 10 | 100 | 68 | 101 |
| 4 | LaCl$_3$ | 200 | 4 | 14.7 | 13.8 | 10 | nd | traces | 101 |
| 5 | La$_2$O$_3$ | 200 | 4 | 12.7 | 13.8 | 10 | nd | traces | 101 |
| 6 | La(NO$_3$)$_3$.6H$_2$O | 200 | 4 | 17.2 | 14.0 | 10 | 40 | 23 | 101 |
| 7 | CF$_3$SO$_3$H | 160 | 6 | 6 | 14.1 | 10 | 90 | 50 | 101 |
| 8[d] | CeO$_2$ (C) | 200 | 5 | 0.15 | 430 | – | 100 | 70 | 103 |
| 9[d] | CeO2 (NC) | 180 | 1 | 0.03 | 430 | – | 100 | 90 | 103 |
| 10 | ZnO-NPs/NBu$_4$Cl | 100 | 7 | [e] | 30 | 17 | 100 | 95 | 105 |
| 11 | Chlorite | 200 | 6 | 70 | 14 | 10 | 99 | 98 | 106 |

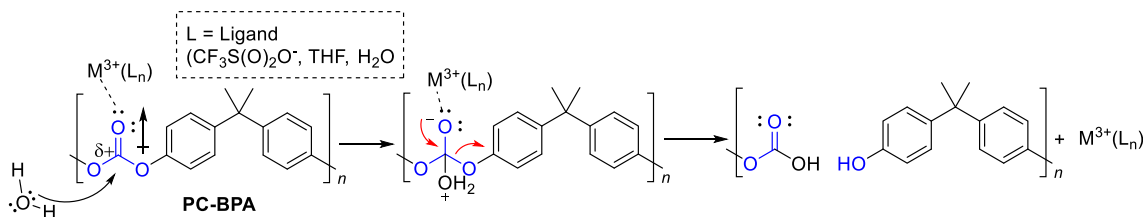[a]Catalyst/PC-BPA weight ratio.
[b]H$_2$O/PC-BPA molar ratio.
[c]THF/PC weight ratio.
[d]C = 75 nm crystallite size; NC = 7.4 nm crystallite size.
[e]ZnO/PC-BPA ≈ 5 mol%, NBu$_4$Cl (5 mol%); nd = not determined.

**SCHEME 15** Proposed mechanism for the hydrolysis of PC-BPA mediated by earth metal triflates.

viable and industrially applicable protocols. In this line, the use of organic solvents and inorganic bases as additives remains the most practical and affordable alternative.

# 5 | DEPOLYMERIZATION BY ALCOHOLYSIS REACTIONS

Alcoholysis of PC-BPA is a simple and economical chemical recycling method that allows the recovery of both, BPA monomer for reuse and the carbonyl group. This avoids the generation of $CO_2$ and allows the use of PC-BPA as a source of the carbonyl group in replacement of more expensive and/or dangerous reagents such as phosgene and its derivatives. In this way, with the use of a suitable alcohol, a variety of carbonates and cyclocarbonates of great importance can be obtained. Being a rigid hydrophobic polymer, PC-BPA is insoluble in most alcohols. Therefore, as in hydrolysis reactions, high temperatures or the use of additives and/or auxiliary solvents are required to carry out depolymerization by alcoholysis. The use of these conditions is necessary to homogenize the PC-BPA and the alcohol system, and activate the carbonyl group. To facilitate a logical and clear presentation, this section has been separated into methanolysis and polyolysis and the additives employed were grouped into inorganic and organic bases (using organic solvents), ionic liquids and deep eutectic solvents, and metals.
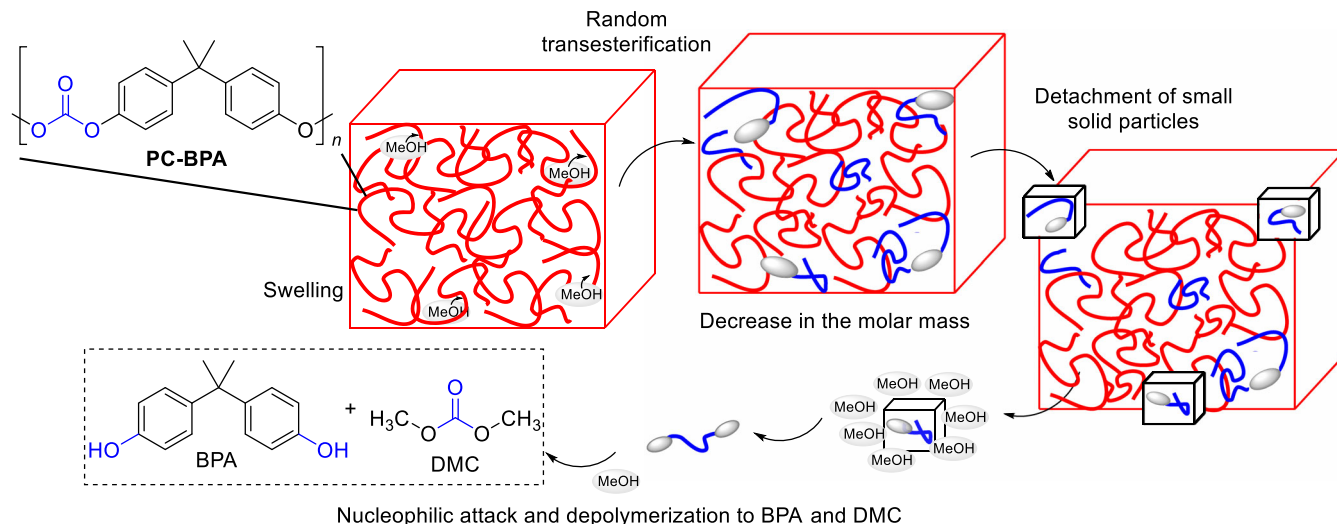
## 5.1 | Methanolysis of PC-BPA

### 5.1.1 | Methanolysis of PC-BPA without auxiliary solvent

Due to the fact that PC-BPA is almost insoluble in simple alcohols, its degradation in MeOH as solvent occurs only at high temperatures. BPA and dimethyl carbonate (DMC) yields close to 80% were obtained when the reaction was carried out at 180°C for 2 h, using a MeOH/PC-BPA molar ratio of 71.[107,108] Similarly, 94% BPA yield was achieved at 190°C (microwave heating), at a pressure of 3.0 MPa for 3 h.[109] Furthermore, with the use of NaOH

(2 g L$^{-1}$ at a flow rate of 0.3 L h$^{-1}$) as an additive, BPA and DMC were significantly formed at a temperature only above 100°C and pressures close to 9 MPa.[110] Similarly, depolymerization by ethanolysis of PC-BPA occurs at 290°C for 50 min (super-critical conditions), yielding 90% of BPA, and 89% of diethyl carbonate (DEC).[111] Kim and co-workers proposed that methanolysis without auxiliary solvent occurs by a mechanism involving three reaction steps.[107] First, MeOH penetrates the PC-BPA polymer (swelling) and produces random transesterifications (bulk erosion). These polymer chain cleavages lead to a decrease in the molar mass of the polymer and the detachment of small solid particles (insoluble) composed of oligomers (monomeric units: 6–7). Then, the nucleophilic attack of MeOH on the oligomer particles produces new scissions generating small soluble oligomers (monomeric units: 2–3). Finally, homogeneous phase transesterifications of soluble oligomers generate BPA and DMC (Scheme 16).[107]

### 5.1.2 | Methanolysis of PC-BPA promoted by inorganic and organic bases in organic solvents

In contrast to solvent-free methanolysis, quantitative formation of DMC and 96% of BPA was obtained when the reaction was carried out at only 60°C for 1.15 h in a MeOH/toluene mixture (1/1) (5 mol of MeOH per mol of carbonate group) in the presence of NaOH (8.5 mol% for each C-O bond to be cleaved). A similar increase in the methanolysis rate was observed with dioxane as solvent.[112] Similarly, Ge and co-workers reported that the use of organic solvents (dioxane, THF, *N*-methyl-2-pyrrolidone, or 1,2-dichloroethane) and NaOH promote the methanolysis of PC-BPA under mild conditions.[91] The time required for the quantitative formation of BPA was observed to be 35, 25, and 20 min when the depolymerization reaction was carried out at 40, 50 and 65°C, respectively, using 8 equiv. of MeOH per carbonate group, 12 mol% of NaOH (referred to the monomer of PC-BPA) as catalyst and THF/PC-BPA ratio of 2 as solvent. The formation of DMC was not determined. Interestingly, a decrease in the reaction time needed to

**SCHEME 16**  Proposed mechanism for the methanolysis of PC-BPA

achieve quantitative conversion was observed when the reaction was performed under ultrasound irradiation.[113] This increase in the methanolysis rate and the softening of the reaction conditions could be interpreted as a decrease of the induction period (swelling, random transesterification) caused by the solvent and/or ultrasound.

Tartaro and co-workers reported that the use of the organic base DBU for promoting the methanolysis of PC-BPA under mild conditions.[114] Quantitative yields of DMC and BPA were obtained when depolymerization was carried out at 100°C for 0.5 h in MeOH as solvent, using 37 equiv. of MeOH per carbonate group and 10 mol % of the catalyst. Lower catalyst loadings or lower reaction temperatures slowed down the reaction. When the reaction was performed with DABCO (1,4-diazabicyclo[2.2.2]octane) or DMAP (4-[dimethylamino]pyridine) as organic catalysts, longer reaction times (2 h and 3.25 h, respectively) were observed. Concentration of the reaction and washing of the residue with ethyl ether produced a solid consisting of the BPA-DBU adduct, whose BPA/DBU molar ratio is close to 2.5. It was observed that the adduct can be reused as a catalyst in successive runs with a slight decrease of its catalytic activity. Similar results were observed when the catalyst was reused by successive additions of fresh PC-BPA after each reaction. This decrease in activity may be due to the increase in the concentration of BPA and, hence, the decrease in the concentration of frees DBU.[114]

The methanolysis reaction was faster than ethanolysis, and when PC-BPA was reacted with an equimolar mixture of MeOH and ethanol, the main product observed was DMC. Nevertheless, ethyl methyl carbonate was obtained in a 60% yield when the depolymerization was carried out at 100°C for 2.5 h, using 1.6 equiv. of MeOH and 24.5 equiv. of EtOH per carbonate group and

10 mol% of the DBU as a catalyst. Wood and co-workers reported that tetramethylammonium methyl carbonate (1.4 mol%) promotes the methanolysis depolymerization of PC-BPA when the reaction was performed in 2-methyl tetrahydrofuran (2-Me-THF) or DMC at 75°C for more than 3 h.[115]

The group of Kim screened the catalytic activity of several additives of known efficacy in transesterification reactions.[116] Methanolysis depolymerization was carried out in 2-Me-THF as solvent at room temperature for 12 h, using 2 mol% of the additive and 10 equiv. of MeOH (Table 4). Neither proton donor acids (p-TsOH) nor conventional Lewis acids (Ti(OiPr)₄, Zn(TAC)) show catalytic activity in the methanolysis reaction (Table 4, entries 1–3). The organic base DMAP was also ineffective in promoting the reaction, and DBU and MTBD showed moderate activity (Table 4, entries 4, 6, and 7). It is worth noting that DMAP showed catalytic activity when the reaction was carried out under microwave heating. A 99% BPA and 69% DMC yields were obtained when the reaction was performed at 180°C (microwave heating) for 5 min with 5 mol% DMAP (Table 4, entry 5).[117] On the other hand, alkaline bases (NaOH and KOH) possess a good catalytic activity and acceptable selectivity. Under these reaction conditions, 84%–87% of DMC, 85%–88% of BPA, and 12%–15% of its mono-methyl carbonate were obtained (Table 4, entries 7 and 8).[118]

Excellent performance and selectivity (98% yield of BPA and DMC) were observed when 1,5,7-triazabicyclo[4.4.0]-dec-5-ene) (TBD) was used as an additive (Table 4, entry 9). Ethanolysis was slower than methanolysis and the reaction had to be carried out at 50°C to achieve a yield of 72% DEC and 71% BPA. In addition, the catalytic activity decreased when no cosolvent was used, or when DMC was used instead of 2-Me-THF. It is noteworthy

**TABLE 4** Methanolysis of PC-BPA.[a]

| Entry | Catalyst | $T$ (°C) | Time (h) | Cat. Load (mol%)[b] | $n_{MeOH}$ / $n_{PC\text{-}BPA}$[c] | PC-BPA conversion (%) | BPA yield (%) | DMC yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | TsOH | r.t | 12 | 2 | 10 | 0 | 0 | 0 |
| 2 | Ti(OiPr)$_4$ | r.t | 12 | 2 | 10 | 0 | 0 | 0 |
| 3 | Zn(TAC) | r.t | 12 | 2 | 10 | 0 | 0 | 0 |
| 4 | DMAP | r.t | 12 | 2 | 10 | 0 | 0 | 0 |
| 5[d,e] | DMAP | 180 | 0.08 | 5 | 46.2 | 100 | 99 | 69 |
| 6 | DBU | r.t | 12 | 2 | 10 | 100 | 40 | 35 |
| 7[f] | MTBD | 50 | 6 | 2 | 10 | 99 | 66 | nd |
| 7 | NaOH | r.t | 12 | 2 | 10 | 100 | 85 | 84 |
| 8 | KOH | r.t | 12 | 2 | 10 | 100 | 88 | 87 |
| 9 | TBD | r.t | 12 | 2 | 10 | 100 | 98 | 98 |

[a]2-Me-THF was used as solvent.
[b]based on the repeating unit of PC-BPA.
[c]MeOH/PC-BPA molar ratio.
[d]see reference 117.
[e]no auxiliary solvent was used.
[f]DMC was used as solvent.

that in DMC, PC-BPA degradation efficiency and selectivity were excellent when the reaction was performed at a higher temperature for less time (50°C for 6 h and 75°C for 2 h). Moreover, TBD can be reused when recovered as its BPA-TBD adduct, or in successive aggregates of more PC-BPA; showing a slight loss of its catalytic activity with each reaction cycle.

Guanidine bases such as TBD can promote transesterification by acting as a nucleophile and/or as a base.[119,120] In nucleophile catalysis, the catalyst attacks the carbonate group and forms an activated carbamate intermediate, which it then transfers to the nucleophile (Scheme 17, a). In the basic catalysis, the catalyst activates the nucleophile through hydrogen bonding that makes the nucleophile more electronegative (Scheme 17, b). In this case, the incipient negative charge on the oxygen of the carbonate group can be stabilized by hydrogen bonding from another alcohol molecule (co-catalyst), the catalyst (TBD) or both (in the scheme, it is shown as stabilized by the catalyst.). It appears that nucleophilic catalysis is the predominant pathway in TBD-catalyzed PC-BPA methanolysis. In addition, by the donor and acceptor property of guanidine, TBD can be expected to facilitate the addition of the incoming alcohol to the carbamate by activating the O—H bond.[118]

### 5.1.3 | Methanolysis of PC-BPA promoted by ionic liquids and deep eutectic solvents

As observed in hydrolysis, ILs were active in the methanolysis of PC-BPA. When imidazolium-based ILs were used as additives, it was observed that their cationic and anionic nature had a significant effect on their catalytic activity (Scheme 18). Under similar reaction conditions, 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) (96% yield of BPA and DMC) showed much more activity than 1-octyl (6% BPA, 6% DMC), 1-benzyl (0% BPA, 0% DMC), 1-allyl (28% BPA, 30% DMC), and 1-(2-chloroethyl) (0% BPA, 0% DMC) derivatives (Table 5, entries 1–5). Methanolysis depolymerization was not observed when 1-ethylpyridin-1-ium bromide was used as additive. Similarly, with chloride as counterion, better catalytic activity was observed than when the counterions were BF$_4^-$ ([Bmim][BF$_4$]) or PF$_6^-$ ([Bmim][PF$_6$]). When the methanolysis was carried out at 105°C for 2 h using a weight ratio of $m_{PC\text{-}BPA}$:$m_{CH3OH}$:$m_{[Bmim][Cl]}$ = 2:3:2 (12 mol of MeOH and 11 mol of IL per mol of monomer), the conversion of PC-BPA was quantitative, and the yields of both BPA and DMC were over 95%. The IL can be reused without an obvious decrease in its catalytic activity.[121] The use of 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) ($m_{IL}$:$m_{PC\text{-}BPA}$ = 0.5:1), in presence of MeOH ($m_{MeOH}$:$m_{PC\text{-}BPA}$ = 0.75:1) results in a 95% yield of BPA when the mixture was heated at 90°C for 2.5 h. Similar BPA yield was obtained when [Bmim][Ac] was used as a catalyst ($m_{IL}$:$m_{PC\text{-}BPA}$ = 0.05:1) and the reaction was carried out in THF ($m_{THF}$:$m_{PC\text{-}BPA}$ = 1:1) as solvent at 105°C.[122]

With the aim of developing an inexpensive, stable, and highly active catalyst for the methanolysis depolymerization of PC-BPA, several ILs with different Lewis acidity and basicity were evaluated (Scheme 18, Table 5).[123,124] The best catalytic activity was found
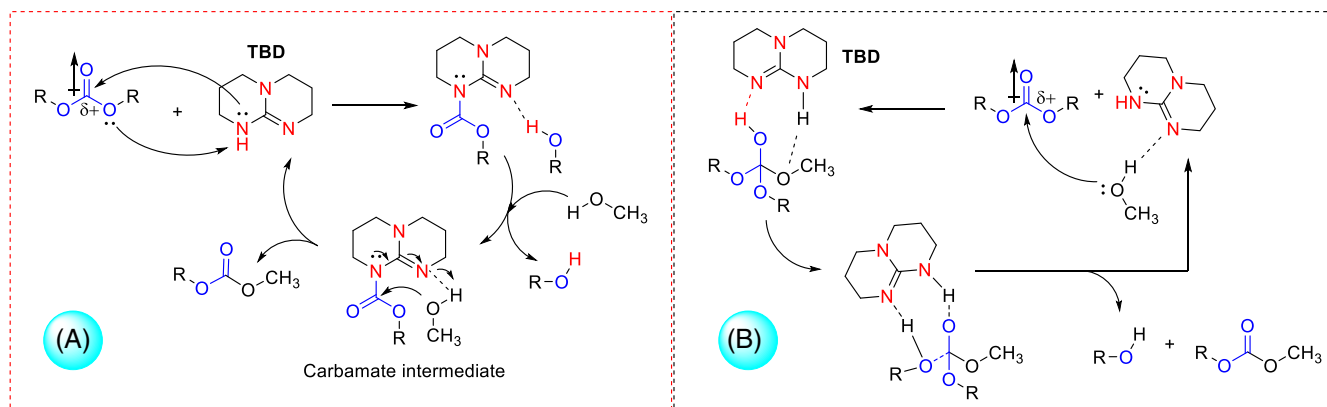
**SCHEME 17** Simplified mechanism for TBD-catalyzed methanolysis of PC-BPA
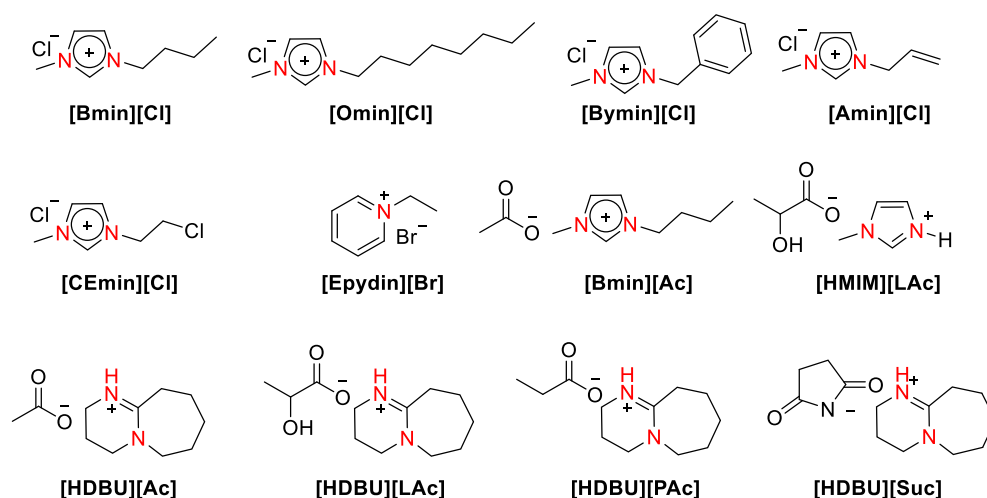


**SCHEME 18** Major IL-based catalysts employed for depolymerization of PC-BPA by methanolysis reactions.

[Bmin][Cl]

[Omin][Cl]

[Bymin][Cl]

[Amin][Cl]

[CEmin][Cl]

[Epydin][Br]

[Bmin][Ac]

[HMIM][LAc]

[HDBU][Ac]

[HDBU][LAc]

[HDBU][PAc]

[HDBU][Suc]

when succinimide/DBU-based ILs were used. Complete PC-BPA methanolysis and a 96% BPA yield were obtained by performing the reaction at 70°C for 2 h, using a catalyst molar ratio of 0.3 in the absence of organic solvents (Table 5, entry 14).

In all systems catalyzed by ILs the rate-determining step for PC-BPA depolymerization appears to be the dissolving or swelling of the PC-BPA. Furthermore, the methanolysis of PC-BPA would occur through the mechanism of bulk erosion. Lactic or succinimide/DBU-based ILs play a dual role: as a solvent, dissolving or swelling the PC-BPA, and as a catalyst, they promoted the simultaneous activation of the carbonate group (electrostatic interaction) and the $CH_3OH$ (hydrogen bond) (Scheme 19).

The ILs were also combined with Lewis acids to evaluate the possible synergy of their catalytic activities in the alcoholysis of PC-BPA.[125] (Table 5, entries 15–17). Like it was observed in hydrolysis, the combination of ZnO-NPs with 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) or tetraalkylammonium chloride promotes the alcoholysis, obtaining BPA in 99% and 100% yields, respectively. PC-

BPA depolymerization with ZnO/NBu₄Cl (Table 5, entry 18) was applied using other alcohols and linear carbonates of phenol, naphthol, and benzyl alcohol were obtained in yields greater than 97%.[105]

Choline chloride (ChCl) and imidazolium-based deep eutectic solvents (DESs) were evaluated as a catalyst in the methanolysis of PC-BPA.[126,127] As observed when used individually, the use of protic acids (*p*-toluenesulfonic acid, oxalic acid, benzoic acid, and succinic acid) (acidic DESs) or neutral additives (glucose and glycerol) (neutral DESs) as the hydrogen bond donors component in the DES shows no catalytic activity to promote depolymerization. Although PC-BPA was degraded to oligomers when Lewis acids DESs (manganese chloride and cupric chloride) were used, BPA was not observed (Table 6, entries 2 and 3). However, basic DESs derived from aniline ([EmimOH]Cl-2AN) and urea ([Ch] or [EmimOH]Cl-2Urea) catalyzed the methanolysis of PC-BPA, and BPA was obtained higher than 99% yield (Table 6, entries 4, 6, and 7). The best performance was observed when urea/imidazolium-based DES ([EmimOH]Cl-2Urea) was used as catalyst (Table 6, entry 7). It was

**TABLE 5** IL-based catalysts for methanolysis of PC-BPA

| Entry | Catalyst | $T$ (°C) | Time (h) | IL (mol%)[a] | $n_{MeOH}$/$n_{PC-BPA}$[b] | PC-BPA conversion (%) | BPA yield (%) | DMC yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | [Bmim][Cl] | 105 | 2.5 | 144 | 12 | 100 | 95.6 | 96.5 | 118 |
| 2 | [Omim][Cl] | 105 | 2.5 | 160 | 12 | 12.1 | 5.7 | 6.1 | 118 |
| 3 | [Bymim][Cl] | 105 | 2.5 | 180 | 12 | 0 | 0 | 0 | 118 |
| 4 | [Amim][Cl] | 105 | 2.5 | 237 | 12 | 38.1 | 28.5 | 30.0 | 118 |
| 5 | [CEmim][Cl] | 105 | 2.5 | 207 | 12 | 0 | 0 | 0 | 118 |
| 6 | [Bmim][Ac] | 90 | 2.5 | 60 | 6 | 100 | 95.5 | nd | 119 |
| 7[c] | [Bmim][Ac] | 105 | 2.5 | 6 | 12 | 100 | 95.4 | nd | 119 |
| 8 | DBU | 100 | 0.5 | 10 | 36 | 100 | 99f | 99 | 111 |
| 9 | [HMIM][LAc] | 120 | 2 | 0.8 | 5 | 100 | 96 | nd | 120 |
| 10 | [HDBU][Ac] | 120 | 1 | 0.8 | 5 | 100 | 98 | nd | 120 |
| 11 | [HDBU][LAc] | 120 | 1 | 0.8 | 5 | 100 | 99 | nd | 120 |
| 12 | [HDBU][LAc] | 90 | 2.5 | 0.8 | 5 | 100 | 98 | nd | 120 |
| 13 | [HDBU][PAc] | 120 | 1 | 0.8 | 5 | 100 | 98 | nd | 120 |
| 14 | [HDBU][Suc] | 70 | 2 | 30 | 6 | 100 | 96 | nd | 121 |
| 15 | [Bmim]Cl·2.0FeCl$_3$ | 120 | 3 | 5 | 6 | 100 | 97.2 | nd | 122 |
| 16[d] | [Bmim]Cl·2.0FeCl$_3$ | 120 | 3 | 5 | 6 | 95.1 | 87.3 | nd | 122 |
| 17[e] | [Bmim]Cl·2.0FeCl$_3$ | 120 | 3 | 5 | 6 | 70.8 | 64.4 | nd | 122 |
| 18 | ZnO-NPs/NBu$_4$Cl | 100 | 7 | 5 | 28 | 100 | nd | 99 | 102 |

[a]Based on the repeating unit of PC-BPA;
[b]MeOH/PC-BPA molar ratio;
[c]THF/PC-BPA weight ratio of 1 was used;
[d]ethanol was used in the alcoholysis reaction;
[e]n-propanol was used in the alcoholysis reaction; nd = not determined.

**SCHEME 19** Proposed action of lactic or succinimide/DBU-based ILs in the methanolysis of PC-BPA
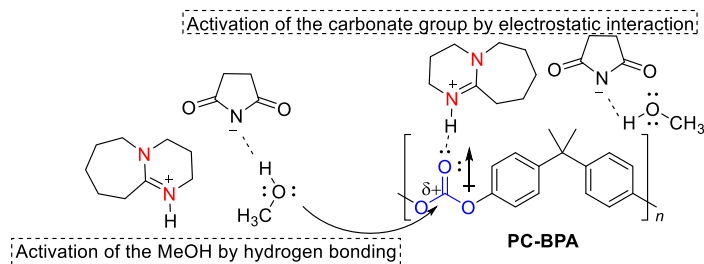


proposed that the basic component of DES (aniline or urea) forms a hydrogen bond with MeOH. This increases the electronegative character of the oxygen atom in MeOH, facilitating nucleophilic attack and PC-BPA depolymerization (Scheme 20).

## 5.1.4 | Methanolysis of PC-BPA promoted by metals

Enthaler and co-workers studied whether alkali metal halides can promote methanolysis depolymerization.[128] The hypothesis was that a simple ion pair could act as a Lewis acid, activating the carbonyl group by electrostatic interaction and/or as a base, increasing the nucleophilicity of the alcohol by hydrogen bond. Surprisingly, KF, KBr, KI, NaI, NaBr, LiBr, and LiCl were all found to produce quantitative depolymerization of the PC-BPA (selectivity to BPA was assumed) and good DMC yields when the reaction was carried out at 180°C under microwave heating for 5–10 min (Table 7).[128] No catalytic activity was observed when NaCl and NaF were used as additives (Table 7, entries 8 and 9). In addition, KF, KI, and NaI showed catalytic activity to promote PC-BPA phenolysis.[129]

The durability and reusability virtues of heterogeneous catalysts were explored in PC-BPA methanolysis.

**TABLE 6** DES as catalysts for methanolysis of PC

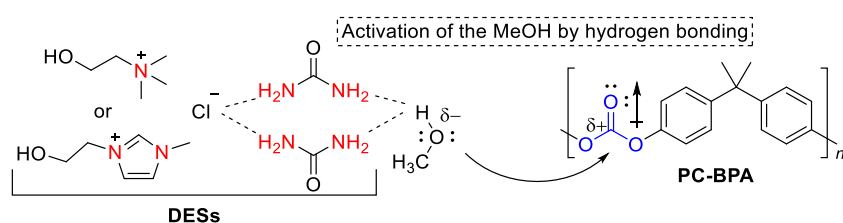| Entry | Catalyst | $T$ (°C) | Time (h) | $m_{DES}/m_{PC\text{-}BPA}$[a] | $n_{MeOH}/n_{PC\text{-}BPA}$[b] | PC-BPA Conversion (%) | BPA Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | ChCl | 130 | 3 | 0.054 | 15 | 88.5 | 88.4 |
| 2 | ChCl-2MnCl$_2$ | 130 | 3 | 0.1 | 15 | 82.6 | – |
| 3 | ChCl-2CuCl$_2$ | 130 | 3 | 0.1 | 15 | 77.9 | – |
| 4 | ChCl-2Urea | 130 | 2.5 | 0.1 | 5 | 100 | 99.8 |
| 5 | [EmimOH]Cl | 120 | 2 | 0.058 | 5 | 0 | 0 |
| 6 | [EmimOH]Cl-2AN | 120 | 2 | 0.1 | 5 | 99 | 95 |
| 7 | [EmimOH]Cl-2Urea | 120 | 2 | 0.1 | 5 | 100 | 99 |

[a]DES/PC-BPA weight ratio;
[b]MeOH/PC-BPA molar ratio.



**SCHEME 20** Proposed action of basic DESs in the methanolysis of PC-BPA

**TABLE 7** Alkali metal halides-based catalysts for methanolysis of PC-BPA

| Entry | Catalyst | $T$ (°C) | Time (min) | Cat. Load (mol%)[a] | MeOH (equiv)[a] | BPA Yield (%)[b] | DMC Yield (%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | KF | 180 | 10 | 2.5 | 46.3 | 99 | 75 |
| 2 | KBr | 180 | 5 | 2.5 | 23.1 | 99 | 52 |
| 3 | KI | 180 | 5 | 2.5 | 23.1 | 99 | 82 |
| 4 | NaI | 180 | 5 | 2.5 | 23.1 | 99 | 83 |
| 5 | NaBr | 180 | 5 | 2.5 | 23.1 | 99 | 87 |
| 6 | LiBr | 180 | 5 | 2.5 | 23.1 | 99 | 63 |
| 7 | LiCl | 180 | 5 | 2.5 | 23.1 | 99 | 77 |
| 8 | NaF | 180 | 10 | 2.5 | 23.1 | <1 | <1 |
| 9 | NaCl | 180 | 10 | 2.5 | 23.1 | <1 | <1 |

[a]Based on the repeating unit of the PC-BPA.
[b]The yield was determined by $^1$H NMR and BPA selectivity was assumed.
[c]Yield was determined by $^1$H NMR relative to BPA.

Liu and co-workers investigated the activity of alkali earth metal oxides (BaO, SrO, and CaO) impregnated on SBA-15 mesoporous molecular sieves.[130] It was observed that 10% CaO/SBA-15 (30 wt%) had the highest catalytic activity, and the BPA yield was over 96% when the reaction was carried out at 130°C for 3 h in THF as solvent and a MeOH molar ratio of 8 (Table 8, entry 1).[130] To increase the catalytic activity through the synergy between CaO and CeO, the same group synthesized a heterogeneous catalyst CaO/CeO-SBA-15 with varying percentages of CaO. However, no significant increase in the catalytic activity of the catalysts was achieved (Table 8, entry 2).[131] The use of calcium-functionalized mesoporous γ-alumina as catalyst, and three-dimensional mesoporous silica foam as CaO support was also studied (Table 8, entries 3 and 4).[132,133]

Although the catalytic activity and reusability of the catalyst were increased, auxiliary solvents were still needed to make PC-BPA depolymerization occurs under relatively mild conditions. To address this problem, a catalyst composed of CeO$_2$—CaO nanoparticles deposited on a ZrO$_2$ nanostructure was synthesized. This catalyst has

**TABLE 8** Heterogeneous catalysts for methanolysis of PC-BPA

| Entry | Catalyst | $T$ (°C) | Time (h) | $m_{Cat}$ / $m_{PC\text{-}BPA}$[a] | $n_{MeOH}$ / $n_{PC\text{-}BPA}$[b] | $m_{THF}$ / $m_{PC\text{-}BPA}$[c] | PC-BPA conversion (%) | BPA yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 10%CaO/SBA-15 | 130 | 3 | 0.33 | 8 | 7 | 100 | 96.8 | 130 |
| 2 | 10%CaO/CeO-SBA-15 | 130 | 3 | 0.3 | 8 | 1.5 | 100 | 94.5 | 131 |
| 3 | Ca-Al$_2$O$_3$ | 130 | 3 | 0.03 | 8 | 1.5 | 100 | 96.3 | 132 |
| 4 | 12%CaO/MCF | 125 | 2.5 | 0.1[d] | 8 | 2 | 100 | 96.4 | 133,137 |
| 5 | 20%CaO-CeO$_2$-ZrO2 | 100 | 2 | 0.05 | 8 | 2 | 100 | 95.8 | 134 |
| 6 | Mg$_3$Al-LDH | 110 | 2 | 0.03 | 5 | – | 100 | 97.2 | 134 |
| 7 | Mg$_3$Al-LDO | 110 | 1 | 0.03 | 5 | – | 100 | 98.3 | 135 |

[a]Catalyst/PC-BPA weight ratio;
[b]MeOH/PC-BPA molar ratio;
[c]THF/PC-BPA weight ratio;
[d]CaO/PC-BPA molar ratio.

more basic active sites on its surface, thus improving the accessibility of reagents and maximizing catalytic activity. This softens the reaction conditions (lower temperature), but does not eliminate the need for a co-solvent (Table 8, entry 5). This catalyst showed high activity, achieving a PC-BPA conversion of almost 100% when 5 wt% was used, when the reaction was carried out at 100°C for 2 h.[134]

Mg/Al-layered double hydroxides (LDHs) (Mg$_3$Al-LDH) and their corresponding layered double oxides (LDOs) (Mg$_3$Al-LDO) showed high activity for PC-BPA methanolysis without the need to use a cosolvent (Table 8, entries 6 and 7).[135] Since the latter two types of the heterogeneous catalysts have strong basic active sites, they can promote the deprotonation of MeOH and the generation of alkoxide ions, which accelerates transesterification and favors methanolysis.

### 5.1.5 | Comparison between hydrolysis and alcoholysis PC-BPA depolimerization

As mentioned above PC-BPA is insoluble in both water and methanol, therefore, depolymerization by hydrolysis or methanolysis must be carried out under harsh reaction conditions. To soften the reaction conditions, additives that activate the carbonyl group and/or nucleophilic and organic solvents are usually added. A direct comparison of methanolysis with hydrolysis cannot be carried out, since the additives, solvents, and reaction conditions tested in the different systems are not the same. It is noted that since MeOH is less polar and more nucleophilic than water, PC-BPA methanolysis conditions are generally milder than hydrolysis conditions. As an example, methanolysis of PC-BPA in MeOH as solvent occurs at 180°C after 2 h,[107] while PC-BPA is stable to hydrolysis at temperature below 265°C.[84] This decrease in reaction temperature prevents the decomposition of BPA into phenol and IPP, making the direct methanolysis of PC-BPA more selective than hydrolysis. On the other hand, it is observed that both chemical depolymerization methods generally behave similarly and that additives (catalysts) that are active in one system are active in the other. Slightly milder conditions are observed in methanolysis. As an example, the same ionic liquids used as catalysts promote hydrolysis at temperatures between 140°C and 160°C,[98,99] while PC-BPA methanolysis occurs at temperatures between 105°C and 120°C.[119,120] Similarly, it was observed that protic acids are inactive in both hydrolysis and methanolysis, and that both systems are promoted by bases and catalysts based on calcium and magnesium, among others.[88,91,112,130]

## 5.2 | Alcoholysis using polyols

The use of different depolymerizing reagents containing hydroxyl groups in the PC-BPA degradation reaction leads to the obtention of different chemical precursors. Scheme 21 summarizes the compounds reported in literature that can be obtained by using different 1,2-, 1,3-, and 1,4-diols.

In particular, regarding the use of 1,2-diols in the controlled degradation of PC-BPA, several studies have been performed using ethylene glycol (**b1**), propylene glycol (**b2**) and glycerol (**b3**) as depolymerization reagents; the results of these works are summarized in Tables 9, 10, and 11, respectively.

In a pioneering work, Kim and co-workers explored the depolymerization of PC-BPA waste using ethylene glycol (**b1**) as reagent (Table 9, entry 1).[136] Yields of BPA of up to 95.6% were achieved using 4 equiv. of **b1** at 220°C (85 min). Despite ethylene carbonate (**d1**) was also formed in these depolymerizations, they reported that the
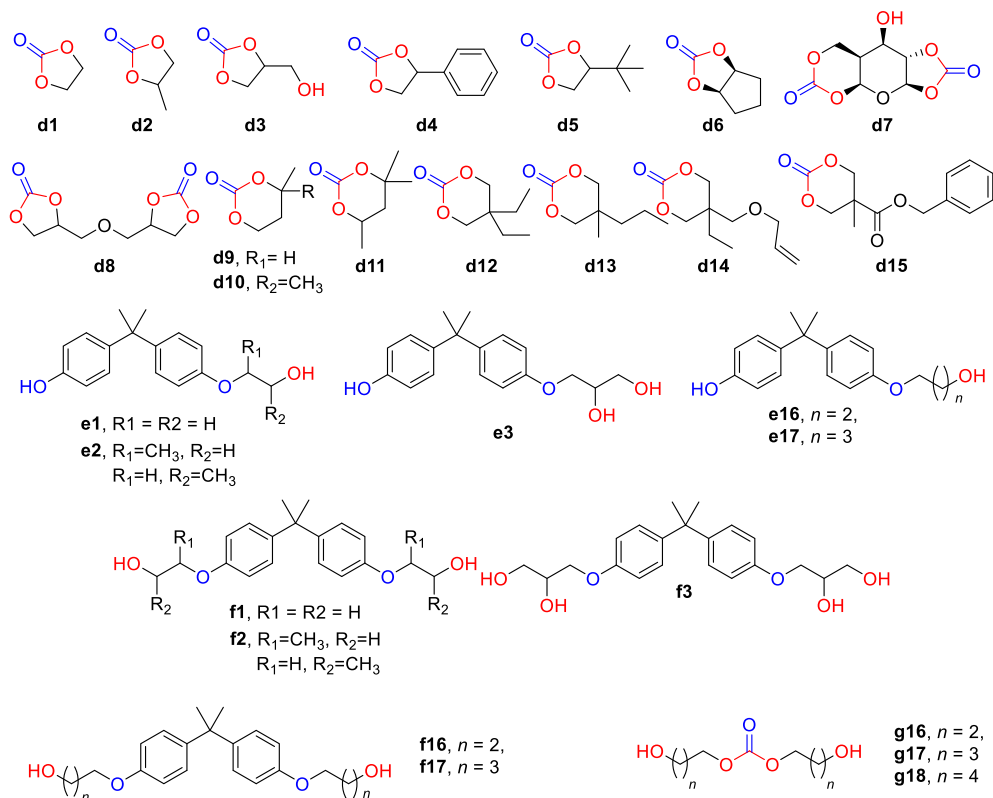
SCHEME 21  Structures of the compounds obtained from PC-BPA depolymerization using different alcohols as depolymerization reagents.

TABLE 9  PC-BPA depolymerization with ethylene glycol (b1)

| Entry | $n_{b1}/n_{PC\text{-}BPA}$ | Catalyst | Cat. Load (mol%) | $T(°C)$ | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| 1[a] | 1:1 | – | – | 220 | 85 | BPA (95.6[b]); d1 (−)[c] | 136 |
| 2[a] | 10:1 | NaOH | 0.1 | 180 | 10 | BPA (42[b]); d1 (−)[c]; e1 (42[b]); f1 (11[b]) | 137 |
| 3[a,d] | 10:1 | NaOH | 0.1 | 180 | 10 | d1 (−)[c]; f1 (100[b]) | 137 |
| 4[e] | 20:1 | NaOH | 2 | 180 | 8 | BPA (92) | 96 |
| 5[f] | 10:1 | NaOH | 3 | 200 | 10 | BPA (31.8); e1 (36.79); f1 (15.3) | 97 |
| 6[f,g] | 10:1 | NaOH/ZnO | 3 | 200 | 20 | BPA (22.3); e1 (45.5); f1 (15.8) | 97 |
| 7[f] | 10:1 | KOH | 3 | 200 | 10 | BPA (29.7); e1 (39.4); f1 (14.4) | 97 |
| 8[f,g] | 10:1 | KOH/ZnO | 3 | 200 | 20 | BPA (19.8); e1 (48.3); f1 (15.1) | 97 |
| 9[f] | 10:1 | CaO | 3 | 200 | 10 | BPA (33.0); e1 (39.8); f1 (12.2) | 97 |
| 10[f,g] | 10:1 | CaO/ZnO | 3 | 200 | 20 | BPA (1.8); e1 (1.5); f1 (63.2) | 97 |
| 11[f] | 10:1 | $Na_2CO_3$ | 3 | 200 | 10 | BPA (14.3); e1 (40.0); f1 (26.5) | 97 |
| 12[g] | 10:1 | $Na_2CO_3$/ZnO | 3 | 200 | 25 | BPA (0); e1 (3.7); f1 (76.5) | 97 |
| 13[h] | 10:1 | $Na_2CO_3$ | 1.9 | 180 | 20 | BPA (27); d1 (−)[c]; e1 (40[b]); f1 (23[b]) | 138 |
| 14[g,h] | 10:1 | $Na_2CO_3$/ZnO | 1.9 | 180 | 140 | d1 (−)[c]; e1 (4[b]); f1 (84[b]) | 138 |
| 15[i] | 5:1 | TBD | 1 | 30 | 720 | BPA (98; 93[a]); d1 (92; 75[a]); | 118 |
| 16[b] | 6:1 | TBD-MSA | 15 | 90 | 240 | BPA (89; 82[a]); d1 (83; 79[a]) | 141 |

[a]Under $N_2$ atmosphere.
[b]Isolated yields.
[c]It was produced although it then decomposed.
[d]Adding ethylene carbonate (d1).
[e]Microwave heating, 3 min (ramp to 180°C), 5 min (hold at 180°C).
[f]Microwave heating, power output 3 kW.
[g]Urea was added.
[h]THF was used as solvent.
[i]2-Me-THF was used as solvent.

**TABLE 10** PC-BPA depolymerization with propylene glycol (**b2**)

| Entry | $n_{b2}/n_{PC-BPA}$ | Catalyst | Cat. Load (mol%) | $T$ (°C) | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | 12:1 | – | – | 180 | 110 | BPA (95); **d2** (94) | 114 |
| 2[a,b] | 14:1 | NaOH | 5 | 100 | 420 | **d2** (75) | 105 |
| 3[c] | 10:1 | $Na_2CO_3$ | 3 | 200 | 10 | BPA (45.3); **e2** (38.2); **f2** (6.8) | 97 |
| 4[c,d] | 10:1 | $Na_2CO_3$/ZnO | 3 | 200 | 20 | BPA (14.2); **e2** (41.2); **f2** (30.5) | 97 |
| 5[b] | 10:1 | $Na_2CO_3$ | 7.9 | 180 | 30 | BPA (23[e]); **d2** (−)[f]; **e2** (54[e]); **f2** (23[e]) | 138 |
| 6[b,d] | 10:1 | $Na_2CO_3$/ZnO | 7.9 | 180 | 210 | **d2** (−)[f]; **e2** (1[e]); **f2** (95[e]) | 138 |
| 7[a,b] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **d2** (98) | 105 |
| 8[a,b] | 14:1 | Pyridine | 5 | 140 | 180 | **d2** (30) | 105 |
| 9[a] | 12:1 | DBU | 10.4 | 180 | 5 | BPA (82); **d2** (84) | 114 |
| 10[a,b] | 1:1 | DBU | 10 | 100 | 150 | BPA (>90); **d2** (99) | 114 |
| 11[a,g] | 5:1 | TBD | 1 | 30 | 720 | BPA (93; 92[e]); **d2** (97; 83[e]) | 118 |
| 12[a] | 3:1 | TBD-MSA | 15 | 130 | 180 | BPA (86); **d2** (90; 87[e]) | 141 |

[a]Under $N_2$ atmosphere.
[b]THF was used as solvent.
[c]Microwave heating, power output 3 kW.
[d]Urea was added.
[e]Isolated yields.
[f]It was produced although it then decomposed.
[g]2-Me-THF was used as solvent.

**TABLE 11** PC-BPA depolymerization with glycerol (**b3**)

| Entry | $n_{b3}/n_{PC-BPA}$ | Catalyst | Cat. Load (mol%) | $T$ (°C) | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| 1[a] | 3:1 | KOH | 6 | 100 | 25 | BPA (100); **d3** (97) | 140 |
| 2 | 4:1 | $Na_2CO_3$ | 0.4 | 170 | 90 | BPA (60.1); **e3** (6.3); **f3** (31.5) | 139 |
| 3[b] | 4:1 | $Na_2CO_3$/ZnO | 0.4 | 170 | 90 | BPA (4.2); **e3** (81.9); **f3** (12.3) | 139 |
| 4[c,d] | 1:1 | DBU | 5 | 60 | 150 | BPA (97); **d3** (>90) | 114 |
| 5[c,d] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 840 | **d3** (>99; 97[e]) | 105 |
| 6[c] | 3:1 | TBD-MSA | 15 | 160 | 120 | **d3** (90; 86[e]) | 141 |

[a]Dioxane was used as solvent.
[b]Urea was added.
[c]Under N2 atmosphere.
[d]THF was used as solvent.
[e]Isolated yields.

cyclic carbonate decomposed into the linear carbonate and $CO_2$. In a similar recent study, Quaranta and co-workers performed the depolymerization reaction of PC-BPA at 180°C but using propylene glycol (**b2**) as depolymerization reagent (Table 10, entry 1).[114] When the reaction was stopped after only 110 min, BPA and cyclic carbonate (**d2**) were obtained in high yields (95 and 94%, respectively).[114]

The NaOH-catalyzed depolymerization of PC-BPA with ethylene glycol (**b1**) produces a mixture of BPA (42%) and BPA ethers (**e1**, 42% and **f1**, 11%) (Table 9, entry 2).[137] The proposed mechanism of this reaction is presented in Scheme 22, and it was suggested that ethylene carbonate (**d1**) is indeed produced, but that it

subsequently reacts with BPA to produce the alkyl-ethers of BPA **e1** and **f1**. When **d1** was added to the reaction mixtures, a higher yield of di-hydroxyethyl ether of BPA (**f1**) was obtained, further supporting the idea that it is, in fact, a reaction intermediate. In addition, **f1** appears as an interesting monomer for the synthesis of other polymer, but industrial viability of such reported process seems to be conditioned to the availability of **d1**, which is not yet a commodity.[137]

Nikje studied the influence of the load of NaOH and of microwave irradiation on the depolymerization of PC-BPA with ethylene glycol (**b1**) (Table 9, entry 4).[96] The author reported that BPA yield improved when
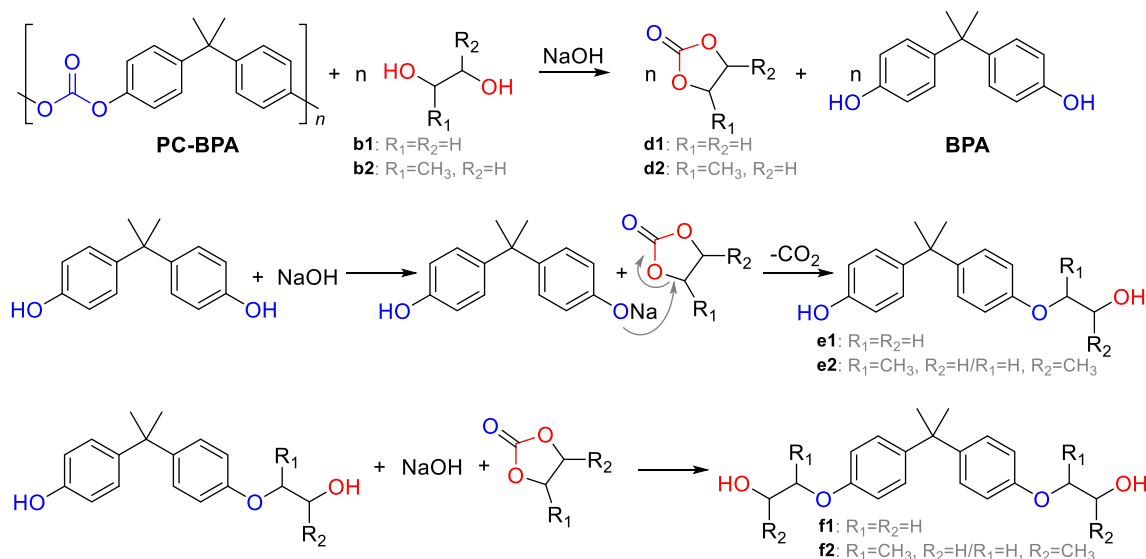
SCHEME 22 Base-catalyzed depolymerization of PC-BPA and the formation of alkyl-ethers of BPA[137]
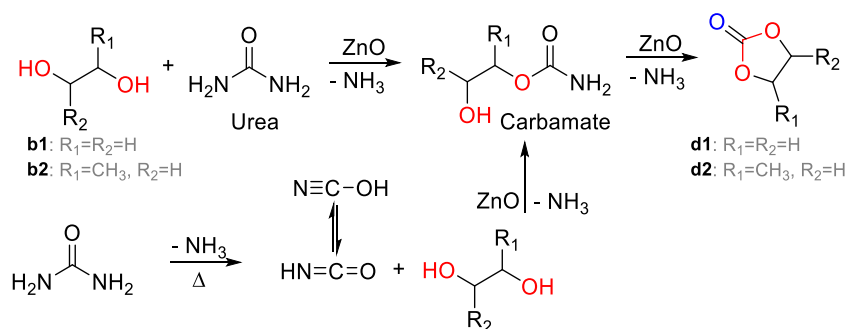


SCHEME 23 Formation of cyclocarbonate compounds by urea addition[138]

increasing catalyst concentration and reaction time. In addition, given the short reaction times required, the authors suggested that microwave energy could be considered as energy source for depolymerization processes.

Dai and co-workers reported the use of $Na_2CO_3$ as basic catalyst for the depolymerization of PC-BPA using both ethylene glycol (**b1**) and propylene glycol (**b2**) (Table 9, entries; Table 10 entry 5).138 Similarly to what is described above, cyclic carbonates **d1** and **d2** were also formed as reaction intermediates. With the aim of increasing the yields of di-ether compounds, after depolymerization, the reaction mixtures were further treated with urea using zinc oxide (ZnO) as catalyst (Table 9, entry 14; Table 10 entry 6). Two possible mechanisms have been proposed to explain the formation of cyclic carbonates (**d1** and **d2**) by the addition of urea, both implying the formation of a carbamate intermediate (Scheme 23). The intermediate could be achieved by the attack of **b1** or **b2** on the carbonyl carbon of urea; or by the thermal decomposition of urea to produce isocyanic acid (HNCO) as an initial step. The cyclic compounds **d1** and **d2** were obtained after an intramolecular reaction;

and could further react with BPA and mono-alkyl ethers of BPA (**e1** or **e2**) in order to increase the yields of di-alkyl -ethers of BPA (**f1** or **f2**).[138]

Frediani and co-workers performed a detailed study of the microwave-assisted depolymerization of PC-BPA using various catalysts and depolymerization reagents (Table 9, entries 4, 5, 7, 9, and 11; Table 10, entry 3; Table 12, entries 15 and 19).[97] In all cases mono-alkyl-ethers of BPA (**e1**, **e2**, **e16**, and **e17**) and di-alkyl-ethers of BPA (**f1**, **f2**, **f16**, and **f17**), BPA and BPA degradation products, were obtained. The effect of the addition of ZnO and urea to the depolymerization reactions in the yield of alkyl-ethers of BPA compounds (**e$_n$** and **f$_n$**) was also studied (Table 9, entries 6, 8, 10, and 12; Table 10 entry 4; Table 12, entries 16 and 20).

Glycerol (**b3**) has also been used for PC-BPA depolymerization, and the effect of the addition of ZnO and urea at the beginning of the reaction was studied.[139] Yields of BPA (4.2%), mono-dihydroxypropyl ether (**e3**, 81.9%) and di-dihydroxypropyl ether (**f3**, 12.3%) of BPA have been obtained under the set of optimized experimental conditions given in Table 11 (entry 3).

**TABLE 12** PC-BPA depolymerization with alcohols

| Entry | $n_{bn}/n_{PC\text{-}BPA}$ | Catalyst | Cat. Load (mol%) | $T$ (°C) | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| | (b4) *Phenylethylene glycol* | | | | | | |
| 1[a] | 5:1 | TBD | 1 | 30 | 720 | BPA (99[b]); **d4** (92[b]) | 118 |
| | (b5) *3,3-dimethylbutane-1,2-diol* | | | | | | |
| 2[a] | 5:1 | TBD | 1 | 30 | 720 | BPA (99[b]); **d5** (96[b]) | 118 |
| | (b6) *Cyclopentane-1,2-diol* | | | | | | |
| 3[a] | 5:1 | TBD | 1 | 30 | 720 | BPA (95[b]); **d6** (89[b]) | 118 |
| | (b7) *Glucose* | | | | | | |
| 4[c] | 3:1 | NaOH | 30 | 110 | 120 | BPA (40); **d7** (38) | 140 |
| 5[d] | 3:1 | NaOH | 30 | 110 | 180 | BPA (42); **d7** (40) | 140 |
| | (b8) *αα′-diglycerol* | | | | | | |
| 6[e] | 3:1 | TBD-MSA | 15 | 160 | 480 | BPA (83[b]); **d8** (84[b]) | 141 |
| | (b9) *butane-1,3-diol* | | | | | | |
| 7[e,f] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **d9** (>99) | 105 |
| 8[e] | 3:1 | TBD-MSA | 15 | 130 | 60 | BPA (97); **d9** (97) | 141 |
| | (b10) *3-methylbutane-1,3-diol* | | | | | | |
| 9[e] | 3:1 | TBD-MSA | 15 | 130 | 180 | BPA (98); **d10** (79) | 141 |
| | (b11) *3-methylpentane-2,4-diol* | | | | | | |
| 10[e] | 3:1 | TBD-MSA | 15 | 130 | 60 | BPA (85); **d11** (86) | 141 |
| | (b12) *2,2-diethylpropane-1,3-diol* | | | | | | |
| 11[e] | 1.5:1 | TBD-MSA | 15 | 130 | 180 | BPA (98); **d12** (79) | 141 |
| | (b13) *2-methyl,2-propyl- propane-1,3-diol* | | | | | | |
| 12[e] | 1.5:1 | TBD-MSA | 15 | 130 | 180 | BPA (98); **d13** (77) | 141 |
| | (b14) *2-([allyloxy]methyl)-2- ethyl-1,3-propanediol* | | | | | | |
| 13[e] | 3:1 | TBD-MSA | 15 | 130 | 60 | BPA (82[b]); **d14** (97;88[b]) | 141 |
| | (b15) *benzyl 3-hydroxy-2-(hydroxymethyl) -2-methylpropanoate* | | | | | | |
| 14[e] | 3:1 | TBD-MSA | 15 | 130 | 180 | BPA (97); **d15** (96) | 141 |
| | (b16) *1,3 propanediol* | | | | | | |
| 15[g] | 10:1 | Na$_2$CO$_3$ | 3 | 200 | 10 | BPA (43.3); **e16** (41.7); **f16** (6.5) | 97 |
| 16[g,h] | 10:1 | Na$_2$CO$_3$ | 3 | 200 | 20 | BPA (39.5); **e16** (38.6); **f16** (10.6) | 97 |
| 17[e] | 6:1 | TBD-MSA | 15 | 130 | 60 | BPA (97); **g16** (97) | 141 |
| 18[e] | 6:1 | TBD-MSA | 15 | 160 | 150 | BPA (>99;92[b]); **g16** (98; 67[b]) | 143 |
| | (b17) *1,4 butanediol* | | | | | | |
| 19[g] | 10:1 | Na$_2$CO$_3$ | 3 | 200 | 10 | BPA (66.4) | 97 |
| 20[g,h] | 10:1 | Na$_2$CO$_3$/ZnO | 3 | 200 | 20 | BPA (40.9); **e17** (10.2); **f17** (14.8) | 97 |
| 21[e] | 6:1 | TBD-MSA | 15 | 160 | 1440 | BPA (94); **g17** (4)[i] | 143 |
| | (b18) *1,5 pentanediol* | | | | | | |
| 22[e] | 6:1 | TBD-MSA | 15 | 160 | 45 | BPA (>99; 79[b]); **g18** (>99; 64[b]) | 143 |

[a]2-Me-THF was used as solvent.
[b]Isolated yields.
[c]DMF was used as solvent.
[d]Pyridine was used as solvent.
[e]Under N$_2$ atmosphere.
[f]THF was used as solvent.
[g]Microwave heating, power output 3 kW;
[h]Urea was added;
[i]THF was obtained as product.
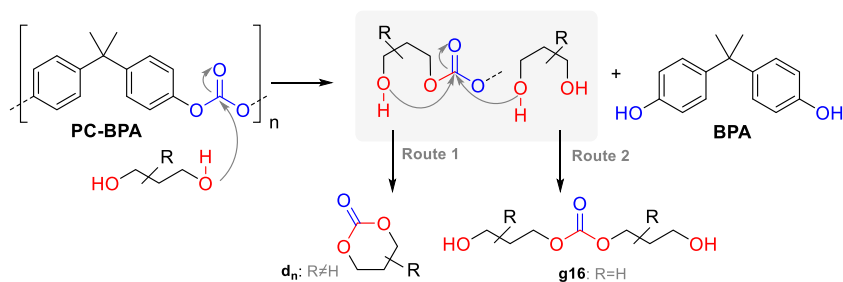
In addition to BPA and BPA ethers, valuable organic carbonates can also be obtained from the depolymerization of PC-BPA. Several authors have studied the depolymerization reaction using different alcohols as depolymerization reagents. In this regard, Oku and co-workers used glycerol (**b3**) and glucose (**b7**) as reagents to afford glycerol carbonate (**d3**) (Table 11, entries 1 and 2) and glucose di-cyclic carbonate (**d7**) (Table 12, entries 4 and 5).140

Despite being inexpensive, alkaline bases cannot be recycled after the depolymerization process, a disadvantage from an environmental viewpoint. In this line, Nacci and co-workers reported a method using IL catalysts.105 The acid/base catalyst employed consisted of ZnO nanoparticles (ZnO-NPs) as Lewis acid, and tetrabutylammonium (NBu₄Cl) (Table 10, entry 7; Table 11, entry 6; and Table 12, entry 7). The reaction was carried out using THF as solvent, and a high excess of 1,2-diols (**b2**, **b3**) and 1,3-diol (**b9**) as depolymerization reagents, obtaining 5-membered (**d2**, **d3**) and 6-membered (**d9**) cyclic carbonates, respectively. It was found that an increase in temperature led to higher conversions, but with lower selectivity. Regarding the catalyst recyclability, ZnO-NPs could be reused up to five 5 times, whereas NBu₄Cl had to be added before each run. For comparative purposes, the use of **b2** as depolymerization reagent and NaOH or pyridine as catalyst, was also studied achieving lower yields (Table 10, entries 2 and 8).105
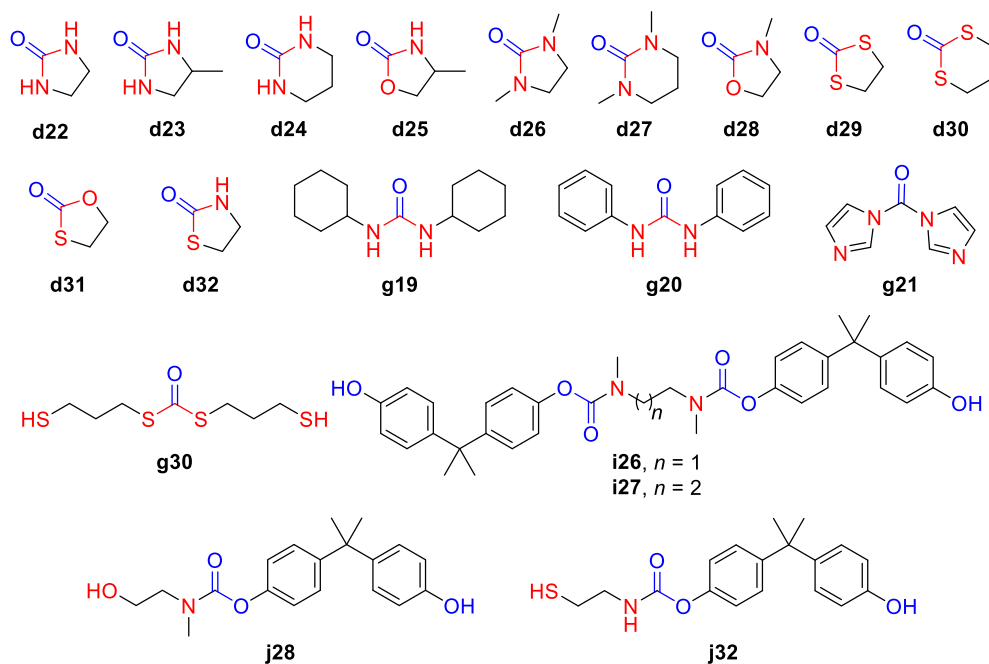
Organic bases proved to be extremely promising catalysts for PC-BPA depolymerizations. For example, DBU successfully catalyzed the depolymerization of PC-BPA using **b2** as depolymerization reagent, with and without solvent (Table 10, entries 9 and 10).114 In the absence of solvent, the depolymerization proceeded faster and by an heterogeneous reaction due to the low solubility of the polymer in the reaction medium. As expected, when the catalyst load was decreased, longer reaction times were required. Cyclic carbonate (**d2**) appears to be stable under the depolymerization reaction conditions and could react with BPA to form the alkyl-ether of BPA compounds (**e2** and **f2**), although only to a smaller extent. Moreover, it was indicated that the catalyst can be recovered and reused. Glycerol (**b3**) can also be employed as depolymerization reagent, which may increase the economic appeal of the process (Table 11, entry 5).

Kim and co-workers explored the use of a guanidine base, TBD, for the mild depolymerization of PC-BPA (Table 9, entry 15; Table 10, entry 11; Table 12, entries 1–3).118 It was found that the donor and acceptor capability of the guanidine functionality of TBD plays an important role in the acceleration of the depolymerization reaction. In this work good yields were achieved for different 5-membered cyclocarbonates such as: ethylene carbonate (**d1**, 89%), propylene carbonate (**d2**, 87%), styrene carbonate (**d4**, 92%), 1-*ter*butyl-propylene carbonate (**d5**, 96%), and cyclopentene carbonate (**d6**, 89%).

A mixture of TBD and methanesulfonic acid (TBD-MSA) has been used recently for the preparation of 5-membered (**d1**, **d2**) and 6-membered (**d9**, **d10**, **d11**, **d12**, **d13**, **d14**, and **d15**) cyclic carbonates and BPA with excellent yields, using PC-BPA and 1,2-diols and 1,3-diols as starting materials (Table 12).141 Indeed, a 5-membered di-cyclic carbonate **d8** was obtained when a di-1,2-diol **b8** was used. It was found that, when the reaction was carried out using 1,3-propanediol (**b16**) as depolymerization reagent, only linear carbonate **g16** was obtained. Instead, when a diol containing a bulky substituent was used as depolymerization reagent, the cyclic product was obtained. On these grounds, two possible routes for depolymerization using 1,3-propanediol derivatives were proposed (Scheme 24). In agreement with the Thorpe-Ingold effect, the presence of bulky substituents would lead to a conformational distortion that promotes the carbonate intramolecular six-membered ring closure (Scheme 24, route 1).141,142 In contrast, the use of no substituents containing 1,3-propanediol **b16**, seems to allow an intermolecular attack of a second molecule of diol producing the linear carbonate **g16** (Scheme 24, route 2).141

Based on these findings, Sardon and co-workers extended the scope of the reaction of PC-BPA to the depolymerization with different aliphatic 1,n-diols, such as 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol, to obtain bis(3-hydroxypropyl) carbonate (**g16**, 98%), bis(4-hydroxybutyl) carbonate (**g17**, 4%), and bis(5-hydroxypentyl) carbonate (**g18**, >99%) and BPA.143 In this work, it was confirmed that a double attack on the carbonate group of PC-BPA (Scheme 24, route 2), is responsible of the formation of linear carbonates (**g16**, **g17**, and **g18**) instead of cyclic ones. Furthermore, an intramolecular

**SCHEME 25** Structures of the compounds obtained from PC-BPA depolymerization using different depolymerization reagents.



**d22**  **d23**  **d24**  **d25**  **d26**  **d27**  **d28**  **d29**  **d30**

**d31**  **d32**  **g19**  **g20**  **g21**

**g30**  **i26**, *n* = 1  **i27**, *n* = 2

**j28**  **j32**

backbiting reaction on the α-carbon of the carbonate group, to afford THF, accounts for the low the yield of the linear carbonate **g17** obtained in the reaction with 1,4-butanediol.

# 6 | DEPOLYMERIZATION BY AMINOLYSIS AND THIOLYSIS REACTIONS

In order to produce compound with urea (-NC[O]N-), carbamate (-NC[O]O-), thiourea (-NC[O]S-), dithiocarbonate (-SC[O]S-) and thiocarbonate (-SC[O]O-) groups, different depolymerization reagents such as monoamines, diamines, aminoalcohols, aminothiols, dithiols and mercaptoalcohols have all been used in the depolymerization reaction of PC-BPA (Scheme 25). The results of these studies are summarized in Table 13.

In a pioneering study, Oku and co-workers performed the reaction employing secondary amines (dimethylamine and diethylamine) as depolymerization reagents, and different catalysts, such as NaOH, ZnCl$_2$, Zn(CH$_3$COO)$_2$, AlCl$_3$ and Al(OC$_2$H$_5$)$_3$, producing a mixture of BPA and carbamates in low yields.[144] They concluded that the transformation of intermediate carbamate into the required tetralkylureas was too slow, and therefore that more drastic reaction conditions would be needed.

The depolymerization reaction was also carried out employing *N,N'*-dimethyl-1,2-diaminoethane (**b26**) in absence of catalyst (Table 13, entries 9 and 10) and using aqueous solutions of Na$_2$CO$_3$ and K$_2$CO$_3$ (Table 13, entries 11–14).[144] In this case, BPA and

1,3-dimethyl-2-imidazolidinone (**d26**) were obtained in good yields. Indeed, **d26** is versatile polar solvent. The reactions were also carried out employing **d26** itself as reaction medium, avoiding the use of conventional solvents. In addition, when *N,N'*-dimethyl-1,3-diaminopropane (**b27**) was used, the corresponding 6-membered cyclic urea **d27** was obtained (Table 13, entry 15). Regarding the depolymerization mechanism, the authors proposed that the first step of the process consists of a bimolecular aminolysis of PC-BPA with the diamine (**b26**, **b27**) to produce an intermediate monoaminocarbamate. An intramolecular nucleophilic attack leads to the formation of the corresponding cyclic urea (Scheme 26, route 1); while an intermolecular attack (Scheme 26, route 2), gives di-carbamate products (**i26**, **i27**).

With the aim of demonstrating the versatility of the methodologies proposed, and that PC-BPA can be utilized as a phosgene equivalent for industrial purposes, the use of different thiols have been studied as depolymerization reagents.[141,145] Furthermore, the thiol-contained compounds obtained are important intermediates in organic and polymer sciences.[32,146,147] In this line, the use of alkanedithioles (1,2-ethanedithiol **b29** and 1,3-propanedithiol **b30**) employing NaOH as catalyst has also been published (Table 13, entries 18, 19, and 21). BPA, as well as the corresponding cyclic (**d29**, **d30**) and linear (**g30**) dithiocarbonates were obtained in these reactions. The authors proposed different depolymerization routes (Scheme 27). The first step implies the reaction of PC-BPA with the conjugate base of the dithiol (**b29**, **b30**) to produce the intermediate products. Cyclic compounds (**d29**, **d30**) are obtained by an intramolecular cyclization of the intermediate (Scheme 27, route 1).

**TABLE 13** PC-BPA depolymerization with monoamines, diamines, aminoalcohols, dithiols, aminothiols and mercaptoalcohols

| Entry | $n_{bn}/n_{PC\text{-}BPA}$ | Catalyst | Cat. Load (mol%) | $T$ (°C) | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| | *(b19) Cyclohexanamine* | | | | | | |
| 1[a,b] | 28:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **g19** (>99) | 105 |
| | *(b20) Aniline* | | | | | | |
| 2[a,b] | 28:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **g20** (>99) | 105 |
| | *(b21) Imidazole* | | | | | | |
| 3[a,b] | 28:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **g21** (>99) | 105 |
| | *(b22) 1,2-ethylene diamine* | | | | | | |
| 4[a] | 6:1 | TBD-MSA | 15 | 90 | 5 | BPA (86[c]); **d22** (96; 92[c]) | 141 |
| | *(b23) Propane-1,2-diamine* | | | | | | |
| 5[a,b] | 14:1 | – | – | 100 | 420 | **d23** (83) | 105 |
| 6[a,b] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **d23** (>99) | 105 |
| | *(b24) propane-1,3-diamine* | | | | | | |
| 7[a,b] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **d24** (>99) | 105 |
| | *(b25) 2-aminopropan-1-ol* | | | | | | |
| 8[a,b] | 14:1 | ZnO-NPs/NBu$_4$Cl | 5 | 100 | 420 | **d25** (>99) | 105 |
| | *(b26) N,N′-dimethyl-1,2-diaminoethane* | | | | | | |
| 9[d] | 1:1 | – | – | 100 | 30 | BPA (87); **d26** (88) | 144 |
| 10[e] | 1:1 | – | – | 100 | 30 | BPA (91); **d26** (93) | 144 |
| 11[d,f] | 1:1 | Na$_2$CO$_3$ | 5 | 100 | 30 | BPA (95); **d26** (94); **i26** (<5) | 144 |
| 12[e,f] | 1:1 | Na$_2$CO$_3$ | 5 | 100 | 30 | BPA (91); **d26** (91) | 144 |
| 13[d,f] | 1:1 | K$_2$CO$_3$ | 5 | 100 | 30 | BPA (90); **d26** (93) | 144 |
| 14[e,f] | 1:1 | K$_2$CO$_3$ | 5 | 100 | 30 | BPA (92); **d26** (92) | 144 |
| | (b27) *N,N′*-dimethyl-1,3-*diaminopropane* | | | | | | |
| 15[d] | 1:1 | – | – | 100 | 90 | BPA (91); **d27** (94); **i27** (<4) | 144 |
| | *(b28) N-methylaminoethanol* | | | | | | |
| 16[d] | 1:1 | – | – | 100 | 90 | BPA (11); **d28** (9); **j28** (89) | 145 |
| 17[d] | 1:1 | NaOH | 3 | 100 | 60 | BPA (97); **d28** (88) | 145 |
| | *(b29) 1,2-ethanedithiol* | | | | | | |
| 18[d,f] | 1:1 | NaOH | 1.5 | 40 | 30 | BPA (90); **d29** (100) | 145 |
| 19[g] | 1:1 | NaOH | 5 | 80 | 210 | BPA (97); **d29** (94) | 145 |
| 20[a] | 3:1 | TBD-MSA | 15 | 90 | 30 | BPA (79[c]); **d29** (89;87[c]) | 141 |
| | *(b30) 1,3-propanedithiol* | | | | | | |
| 21[d,f] | 1:1 | NaOH | 1.5 | 100 | 180 | BPA (96); **d30** (75); **g30** (14) | 145 |
| | *(b31) Mercaptoethanol* | | | | | | |
| 22[d] | 1:1 | NaOH | 1 | 100 | 180 | BPA (92); **d31** (87) | 145 |
| 23[d] | 1:1 | KOH | 1 | 100 | 60 | BPA (100); **d31** (47) | 145 |
| | *(b32) 2-aminoethanethiol* | | | | | | |
| 24[d] | 1:1 | – | – | 100 | 90 | BPA (46); **d32** (47); **j32** (54) | 145 |
| 25[d] | 1:1 | NaOH | 1 | 100 | 60 | BPA (100); **d32** (100) | 145 |

[a]Under N2 atmosphere.
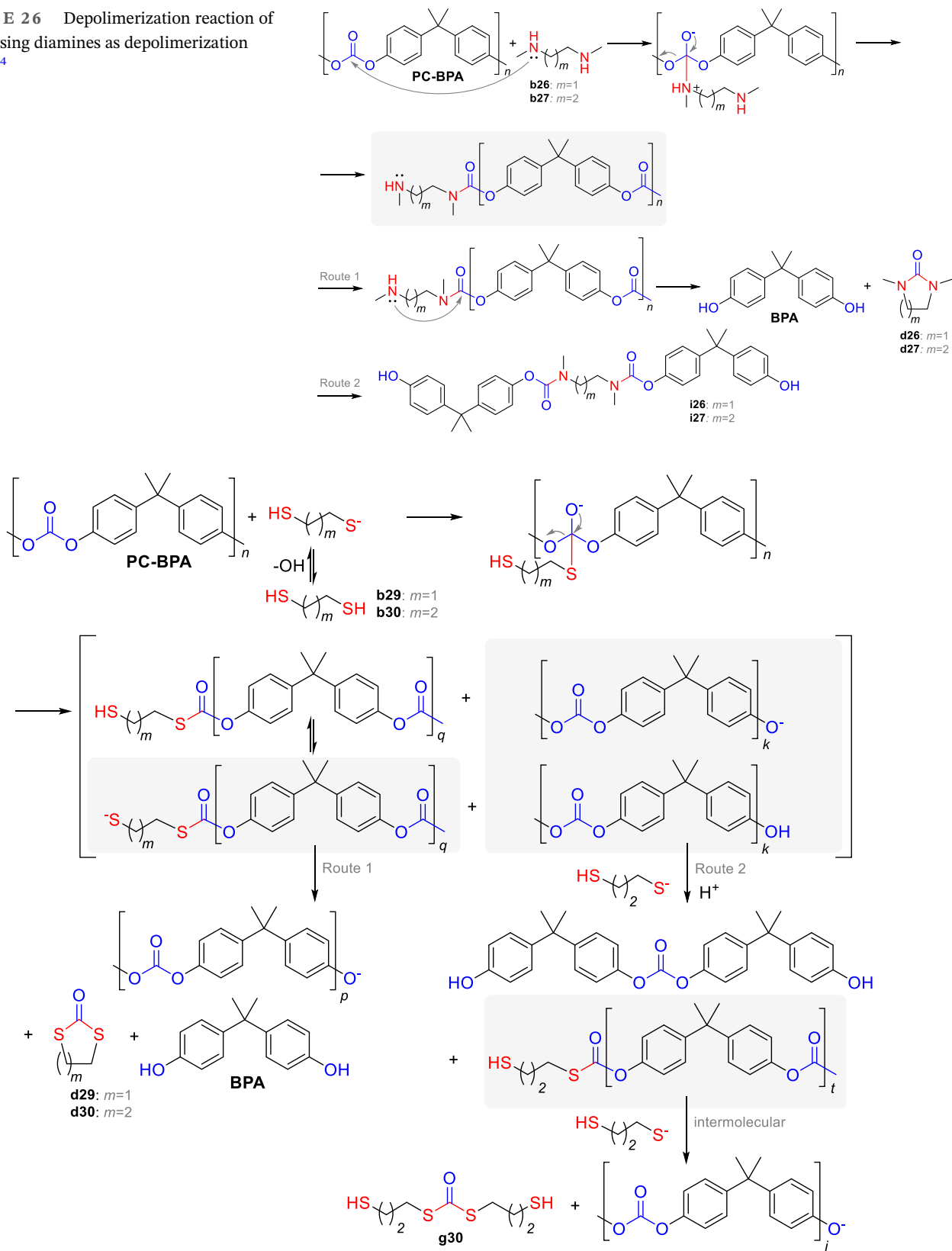[b]THF was used as solvent.
[c]Isolated yields.
[d]Dioxane was used as solvent.
[e]1,3-dimethyl-2-imidazolidinone (d26) was used as solvent.
[f]Aqueous solution.
[g]1,3-dithiolan-2-one (d29) was used as solvent.

**SCHEME 26** Depolimerization reaction of PC-BPA using diamines as depolimerization reagents[144]



**SCHEME 27** Depolimerization reaction of PC-BPA using alkanedithioles as depolimerization reagents[145]

Whereas when using **b30** as depolymerization reagent a linear compound **g30** would also be produced by an intermolecular attack (Scheme 26, route 2).

Mercaptoethanol (**b31**) has been used as depolymerization reagent in combination with different bases as catalyst to yield the corresponding heterocycle

compound (1,3-oxathiolan-2-one **d31**) (Table 13, entries 22 and 23).[145]

The use of aminothiols and aminoalcohols has also been investigated. *N*-methylaminoethanol (**b28**) and 2-aminoethanethiol (**b32**) were used as depolymerization reagents in the reaction with and without catalyst (Table 13, entries 16, 17, 24, and 25). In the absence of catalyst linear compounds (**j28**, **j32**) were obtained.[145] It was reported that the corresponding heterocyclic compounds (*N*-methy1-1, 3-oxazolidine-2-one **d28** and 1,3-thtiazolidine-2-one **d32**) were obtained in good yields when NaOH was used as catalyst.

Acid/based mixture ZnO-NPs/NBu₄Cl has been used as catalyst employing monoamines (**b19**, **b20**), imidazole (**b21**), 1,2-diamines (**b23**) and 1,3-diamines (**b24**) as depolymerization reagents (Table 13, entries 1–3 and 6–8). Linear ureas (**g19**, **g20**, and **g21**), 5-membered cyclic ureas (**d23**) and 6-membered cyclic ureas (**d24**) were obtained. The reported method was also successful with 2-aminopropan-1-ol (**b25**) affording carbamate cyclic **d25** as product.

The TBD-MSA couples were evaluated for the depolymerization of PC-BPA using 1,2-ethylene diamine (**b22**) and 1,2-ethylene dithiol (**b29**) (Table 13, entries 4 and 20) as acyl group acceptor. Thus, BPA, imidazolidin-2-one (**d22**) and 1,3-dithiolan-2-one (**d29**) were obtained in good yields.[141]

# 7 | CONCLUSIONS

Polycarbonate waste can be chemically recycled by several routes, offering an advantageous alternative over mechanical compounding. The resulting products and their yields vary between each route and sub route, depending on the corresponding operating conditions.

Pyrolysis can convert disposed PC into useful chemical products. This process turns the material into different gases, liquid oil and char fractions, which could be employed in several areas, including polymeric industries. Conversion, yields and properties of the obtained products depend on PC composition and pyrolysis conditions, such as reactor type, temperature, heating rate, residence time, and the absence or presence of catalyst (and type). Pyrolysis reaction time and temperature could be lowered, and product distribution could be narrowed by adding a suitable catalyst. However, yields for specific products are still low and several appropriate separation and purification operations are required in order to obtain commercial chemical compounds, thus increasing energy and costs. Apart from BPA and useful solvents, polyphenols may also be obtained with this mechanism, which can be further employed as polymer precursors.

In relation to the hydrogenolysis, excellent results were achieved on the development of new catalytic systems that are not derived from precious metals. However, most of the hydrogenative depolymerization reactions still require relatively harsh reaction conditions and high $H_2$ pressures to reach complete polymer conversions, even using the most reactive catalysts. Although reactions under such conditions are still amenable for the synthesis of high value chemicals, the scaling up of such processes at the ton-scale required to recycle even a small proportion of PC waste appears to be a very challenging task. Thus, further research is needed to develop more amenable processes that are also less energy-demanding and more easily scalable.

After describing the different depolymerization mechanisms in detail, it is concluded that successfully recovering BPA and the carbonate group by hydrolysis, alcoholysis, aminolysis and thiolysis is entirely possible. This way, using PC-BPA waste as a carbonate source (avoiding phosgene and the release of $CO_2$ into the environment) becomes an interesting possibility. Moreover, the use of alcohols, amines, and thiols as depolymerization reagents can lead to the production of different taylor-made compounds (linear and cyclic carbonates of high value such as dimethyl carbonate, ethylene carbonate and glycerol carbonate; ureas, carbamates, thioureas, dithiocarbonates, and thiocarbonates), that can be used for polymer synthesis or as chemical reagents.

## AUTHOR CONTRIBUTIONS
**Elangeni Ana Gilbert**: Visualization (equal); writing – original draft (equal); writing – review and editing (lead). **Mara Lis Polo**: Visualization (equal); writing – original draft (equal); writing – review and editing (equal). **Juan Martín Maffi**: Writing – original draft (equal); writing – review and editing (equal). **Javier Fernando Guastavino**: Supervision (equal); visualization (lead); writing – original draft (lead); writing – review and editing (equal). **Santiago Eduardo Vaillard**: Supervision (equal); writing – original draft (equal).

## ORCID
*Diana Alejandra Estenoz* https://orcid.org/0000-0001-7581-7603

## REFERENCES
[1] E. V. Antonakou, D. S. Achilias, *Waste Biomass Valoriz.* **2013**, *4*, 9.

[2] Polycarbonate Market Analysis By Application (Transportation, Electrical & Electronics, Construction, Packaging, Consumer Goods, Optical Media, Medical Devices) And Segment Forecasts To 2024, San Francisco, **2016**.

[3] V. Serini, *Encycl. Ind. Chem* **2012**, *28*, 603.

[4] C. M. Metz, *Work. Health Saf.* **2016**, *64*, 28.

[5] D. J. Brunelle, *Kirk-Othmer Encycl. Chem. Technol.* **1993**, *19*, 278.

[6] S. Fukuoka, I. Fukawa, T. Adachi, H. Fujita, N. Sugiyama, T. Sawa, *Org. Process Res. Dev.* **2019**, *23*, 145.

[7] P. Wang, J. H. Park, M. Sayed, T. S. Chang, A. Moran, S. Chen, S. H. Pyo, *Polym. Chem.* **2018**, *9*, 3798.

[8] R. Hassan, M. U. A. Khan, A. M. Abdullah, S. I. A. Razak, *Polymers (Basel).* **2021**, *13*, 1.

[9] D. Wu, D. Zhang, S. Liu, Z. Jin, T. Chowwanonthapunya, J. Gao, X. Li, *Chem. Eng. J.* **2020**, *399*, 125878.

[10] D. S. Achilias, A. Giannoulis, G. Z. Papageorgiou, *Polym. Bull.* **2009**, *63*, 449.

[11] P. S. Roy, G. Garnier, F. Allais, K. Saito, *ChemSusChem* **2021**, *14*, 4007.

[12] J. E. Cooper, E. L. Kendig, S. M. Belcher, *Chemosphere* **2011**, *85*, 943.

[13] W. D'Ambrières, in Field Action Science Reports, Vol. 19 (Ed: F. Arnaud), Institut Veolia, Paris, France, 2019, Ch. 1.

[14] D. S. Achilias, L. Andriotis, I. A. Koutsidis, D. A. Louka, N. P. Nianias, P. Siafaka, I. Tsagkalias, G. Tsintzou, in *Material Recycling – Trends and Perspectives* (Ed: D. Achilias), InTech, Rijeka **2012**.

[15] C. Zhuo, Y. A. Levendis, *J. Appl. Polym. Sci.* **2014**, *131*, 1.

[16] N. Singh, D. Hui, R. Singh, I. P. S. Ahuja, L. Feo, F. Fraternali, *Compos. B: Eng.* **2017**, *115*, 409.

[17] I. A. Ignatyev, W. Thielemans, B. V. Beke, *ChemSusChem* **2014**, *7*, 1579.

[18] K. Ragaert, L. Delva, K. Van Geem, *Waste Manage.* **2017**, *69*, 24.

[19] M. Heidarpour, S. O. Movahed, S. Jourabchi, *J. Polym. Environ.* **2021**, *29*, 3130.

[20] M. Censori, F. La Marca, M. T. Carvalho, *Waste Manage.* **2016**, *54*, 39.

[21] V. Luciani, G. Bonifazi, P. Rem, S. Serranti, *Waste Manage.* **2015**, *45*, 118.

[22] H. Wang, Y. Zhang, C. Wang, *Sep. Purif. Technol.* **2019**, *226*, 75.

[23] L. Huang, H. Wang, C. Wang, J. Zhao, B. Zhang, *Waste Manage. Res.* **2017**, *35*, 294.

[24] J. Maris, S. Bourdon, J. M. Brossard, L. Cauret, L. Fontaine, V. Montembault, *Polym. Degrad. Stab.* **2018**, *147*, 245.

[25] M. P. Aznar, M. A. Caballero, J. A. Sancho, E. Francés, *Fuel Process. Technol.* **2006**, *87*, 409.

[26] H. Chen, K. Wan, Y. Zhang, Y. Wang, *ChemSusChem* **2021**, *14*, 4123.

[27] Y. B. Zhao, X. D. Lv, H. G. Ni, *Chemosphere* **2018**, *209*, 707.

[28] J. G. Kim, *Polym. Chem.* **2020**, *11*, 4830.

[29] J. Bozi, Z. Czégény, E. Meszaros, M. Blazso, *J. Anal. Appl. Pyrol.* **2007**, *79*, 337.

[30] E. V. Antonakou, K. G. Kalogiannis, S. D. Stephanidis, K. S. Triantafyllidis, A. A. Lappas, D. S. Achilias, *Waste Manage.* **2014**, *34*, 2487.

[31] R. Miandad, M. A. Barakat, A. S. Aburiazaiza, M. Rehan, A. S. Nizami, *Process Safe. Environ.* **2016**, *102*, 822.

[32] S. C. Kosloski-Oh, Z. A. Wood, S. C. Manjarrez, J. P. de Los Rios, M. E. Fieser, *Mater. Horizons* **2021**, *8*, 1084.

[33] S. D. A. Sharuddin, F. Abnisa, W. M. A. W. Daud, M. K. Aroua, *Energ. Convers. Manag.* **2016**, *115*, 308.

[34] E. Apaydin-Varol, S. Polat, A. Pütün, *Thermal. Sci.* **2014**, *18*, 833.

[35] L. H. Lee, *J. Polym. Sci. Part A* **1964**, *2*, 2859.

[36] A. Davis, J. H. Golden, *Nature* **1965**, *206*(4982), 397.

[37] A. Davis, J. H. Golden, *J. Chem. Soc. B* **1968**, *1*, 45.

[38] R. L. Bartosiewicz, C. Booth, *Eur. Polym. J.* **1974**, *10*, 791.

[39] K. B. Abbås, *Polymer* **1980**, *21*, 936.

[40] G. Montaudo, C. Puglisi, F. Samperi, *Polym. Degrad. Stab.* **1989**, *26*, 285.

[41] G. Montaudo, C. Puglisi, R. Rapisardi, F. Samperi, *Polym. Degrad. Stab.* **1991**, *31*, 229.

[42] G. Montaudo, C. Puglisi, *Polym. Degrad. Stab.* **1992**, *37*, 91.

[43] C. Puglisi, L. Sturiale, G. Montaudo, *Macromolecules* **1999**, *32*, 2194.

[44] G. Montaudo, S. Carroccio, C. Puglisi, *J. Annal. Appl. Pyrol.* **2002**, *64*, 229.

[45] I. C. McNeill, A. Rincon, *Polym. Degrad. Stab.* **1991**, *31*, 163.

[46] I. C. McNeill, A. Rincon, *Polym. Degrad. Stab.* **1993**, *39*, 13.

[47] B. N. Jang, C. A. Wilkie, *Polym. Degrad. Stab.* **2004**, *86*, 419.

[48] J. Huang, C. He, X. Li, G. Pan, H. Tong, *Waste Manage.* **2018**, *71*, 181.

[49] Q. Liu, S. Liu, Y. Lv, P. Hu, Y. Huang, M. Kong, G. Li, *Fuel* **2021**, *287*, 119484.

[50] X. Wei, J. Yu, J. Du, L. Sun, *Energ. Fuels* **2021**, *35*, 5026.

[51] X. G. Li, M. R. Huang, *Polym. Int.* **1999**, *48*, 387.

[52] J. Katajisto, T. T. Pakkanen, T. A. Pakkanen, P. Hirva, *J. Mol. Struct. Theochem.* **2003**, *634*, 305.

[53] B. Janković, *J. Polym. Res.* **2009**, *16*, 213.

[54] Y. Kitahara, S. Takahashi, M. Tsukagoshi, T. Fujii, *Chemosphere* **2010**, *80*, 1281.

[55] E. Apaydin-Varol, S. Polat, A. E. Putun, *Therm. Sci.* **2014**, *18*, 833.

[56] M. N. Siddiqui, H. H. Redhwi, E. V. Antonakou, D. S. Achilias, *J. Anal. Appl. Pyrol.* **2018**, *132*, 123.

[57] M. N. Siddiqui, E. V. Antonakou, H. H. Redhwi, D. S. Achilias, *Thermochim. Acta* **2019**, *675*, 69.

[58] M. Day, J. D. Cooney, C. Touchette-Barrette, S. E. Sheehan, *J. Anal. Appl. Pyrol.* **1999**, *52*, 199.

[59] S. J. Chiu, S. H. Chen, C. T. Tsai, *Waste Manage.* **2006**, *26*, 252.

[60] N. M. M. Mitan, M. Brebu, T. Bhaskar, A. Muto, Y. Sakata, M. Kaji, *J. Mater. Cycles Waste* **2007**, *9*, 62.

[61] D. S. Achilias, E. V. Antonakou, E. Koutsokosta, A. A. Lappas, *J. Appl. Polym. Sci.* **2009**, *114*, 212.

[62] E. V. Antonakou, K. G. Kalogiannis, S. D. Stefanidis, S. A. Karakoulia, K. S. Triantafyllidis, A. A. Lappas, D. S. Achilias, *Polym. Degrad. Stab.* **2014**, *110*, 482.

[63] J. Wang, J. Jiang, X. Wang, R. Wang, K. Wang, S. Pang, Z. Zhong, Y. Sun, R. Ruan, A. J. Ragauskas, *J. Hazard. Mater.* **2020**, *386*, 121970.

[64] J. Wang, J. Jiang, X. Meng, M. Li, X. Wang, S. Pang, K. Wang, Y. Sun, Z. Zhong, R. Ruan, A. J. Ragauskas, *Environ. Sci. Technol.* **2020**, *54*, 8390.

[65] M. Blazsó, *J. Anal. Appl. Pyrol.* **1999**, *51*, 73.

[66] T. Lee, S. Jung, K. Baek, Y. F. Tsang, K. Y. A. Lin, Y. J. Jeon, E. E. Kwon, *J. Hazard. Mater.* **2022**, *423*, 126992.

[67] A. Kumar, C. Gao, *Chem CatChem* **2021**, *13*, 1105.

[68] C. Wang, O. El-Sepelgy, *Curr. Opin. Green Sustain. Chem.* **2021**, *32*, 100547.

[69] A. C. Fernandes, *Green Chem.* **2021**, *23*, 7330.

[70] S. Westhues, J. Idel, J. Klankermayer, *Sci. Adv.* **2018**, *4*, 9669.

[71] T.-O. Kindler, C. Alberti, J. Sundermeier, S. Enthaler, *ChemistryOpen* **2019**, *8*, 1410.

[72] C. Alberti, S. Eckelt, S. Enthaler, *ChemistrySelect* **2019**, *4*, 12268.

[73] E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609.

[74] C. Alberti, J. Kessler, S. Eckelt, M. Hofmann, T.-O. Kindler, N. Santangelo, L. Fedorenko, S. Enthaler, *ChemistrySelect* **2020**, *5*, 4231.

[75] P. Dahiya, M. K. Gangwar, B. Sudararaju, *ChemCatChem* **2021**, *13*, 934.

[76] J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Am. Ethnol.* **1890**, *2017*, 56.

[77] C. Alberti, E. Fedorenko, S. Enthaler, *ChemistryOpen* **2020**, *9*, 818.

[78] X. Liu, J. G. de Vries, T. Werner, *Green Chem.* **2019**, *21*, 5248.

[79] V. Zubar, Y. Lebedev, L. M. Azofra, L. Cavallo, O. El-Sepelgy, M. Rueping, *Angew. Chem. Int.* **2018**, *57*, 13439.

[80] E. Feghali, T. Cantat, *ChemSusChem* **2015**, *8*, 980.

[81] L. Monsigny, J.-C. Berthet, T. Cantat, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10481.

[82] H. Schnell, H. Krimm, *Angew. Chem. Int. Edit.* **1963**, *2*, 373.

[83] H. Tagaya, K. Katoh, J. Kadokawa, K. Chiba, *Polym. Degrad. Stab.* **1999**, *64*, 289.

[84] Z. Pan, I.-M. Chou, R. C. Burruss, *Green Chem.* **2009**, *11*, 1105.

[85] Z. Pan, Z. Hu, Y. Shi, Y. Shen, J. Wang, I.-M. Chou, *RSC Adv.* **2014**, *4*, 19992.

[86] M. Watanabe, Y. Matsuo, T. Matsushita, H. Inomata, T. Miyake, K. Hironaka, *Polym. Degrad. Stab.* **2009**, *94*, 2157.

[87] T. Yoshioka, K. Sugawara, T. Mizoguchi, A. Okuwakiy, *Chem. Lett.* **2005**, *34*, 282.

[88] G. Grause, K. Sugawara, T. Mizoguchi, T. Yoshioka, *Polym. Degrad. Stab.* **2009**, *94*, 1119.

[89] G. Grause, N. Tsukada, W. J. Hall, T. Kameda, P. T. Williams, T. Yoshioka, *Polym. J.* **2010**, *42*, 438.

[90] A. Ikeda, K. Katoh, H. Tagaya, *J. Mater. Sci.* **2008**, *43*, 2437.

[91] F. Liu, Z. Li, S.-T. Yu, X. Cui, C.-X. Xie, X.-P. Ge, *J. Polym. Environ.* **2009**, *17*, 208.

[92] N. Deirrama, A. R. Rahmat, *APCBEE Proc.* **2012**, *3*, 172.

[93] G. P. Tsintzou, D. S. Achilias, *Waste Biomass Valor.* **2013**, *4*, 3.

[94] G. P. Tsintzou, E. V. Antonakou, D. S. Achilias, *J. Hazar. Mater.* **2012**, *241*, 137.

[95] M. M. A. Nikje, M. Askarzadeh, *Polímeros* **2013**, *23*, 29.

[96] M. M. A. Nikje, *Polimery* **2011**, *56*, 381.

[97] L. Rosi, M. Bartoli, A. Undri, M. Frediani, P. Frediani, *J. Mol. Catal. A: Chem.* **2015**, *408*, 278.

[98] X. Song, F. Liu, L. Li, X. Yang, S. Yu, X. Ge, *J. Hazard. Mater.* **2013**, *244*, 204.

[99] L. Li, F. Liu, Z. Li, X. Song, S. Yu, S. Liu, *Fibers Polym.* **2013**, *14*, 365.

[100] M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, *Polym. Degrad. Stab.* **2018**, *157*, 9.

[101] E. Quaranta, *Appl. Catal. B: Environ.* **2017**, *206*, 233.

[102] S. Kobayashi, *Eur. J. Org. Chem.* **1999**, *1*, 15.

[103] M. Taguchi, Y. Ishikawa, S. Kataoka, T. Naka, T. Funazukuri, *Catal. Comm.* **2016**, *84*, 93.

[104] X. Ren, Z. Zhang, Y. Wang, J. Lu, J. An, J. Zhang, M. Wang, J. Zhang, Y. Luo, *RSC Adv.* **2019**, *9*, 15229.

[105] F. Iannone, M. Casiello, A. Monopolia, P. Cotugnoa, M. C. Sportelli, R. A. Picca, N. Cioffia, M. M. Dell'Anna, A. Nacci, *J. Mol. Catal. A: Chem.* **2017**, *426*, 107.

[106] E. Quaranta, E. Mesto, M. Lacalamita, C. Malitesta, E. Mazzotta, E. Scelsi, E. Schingaro, *Waste Manage.* **2021**, *120*, 642.

[107] D. Kim, B.-K. Kim, Y. Cho, M. Han, B.-S. Kim, *Ind. Eng. Chem. Res.* **2009**, *48*, 6591.

[108] H. Tang, Y. Hu, G. Li, A. Wang, G. Xu, C. Yu, X. Wang, T. Zhanga, N. Li, *Green Chem.* **2019**, *21*, 3789.

[109] K. Ikenaga, K. Higuchi, S. Kohri, K. Kusakabe, IOP conf. Ser., *Mater. Sci. Eng.* **2018**, *458*, 012037.

[110] R. Piñero, J. García, M. J. Cocero, *Green Chem.* **2005**, 7, 380.

[111] H. Jie, H. Ke, Z. Qing, C. Lei, W. Yongqiang, Z. Zibin, *Polym. Degrad. Stab.* **2006**, *91*, 2307.

[112] L.-C. Hu, A. Oku, E. Yamada, *Polymer* **1998**, *39*, 3841.

[113] C. S. Bhogle, A. B. Pandit, *Ultrason. Sonochem.* **2019**, *58*, 104667.

[114] E. Quaranta, D. Sgherza, G. Tartaro, *Green Chem.* **2017**, *19*, 5422.

[115] P. McKeown, M. Kamran, M. G. Davidson, M. D. Jones, L. A. Román-Ramírez, J. Wood, *Green Chem.* **2020**, *22*, 3721.

[116] J. Otera, *Chem. Rev.* **1993**, *93*, 1449.

[117] C. Alberti, S. Enthaler, *Waste Biomass Valoriz.* **2020**, *11*, 4621.

[118] T. Do, E. R. Baral, J. G. Kim, *Polymer* **2018**, *143*, 106.

[119] X. Fu, C.-H. Tan, *Chem. Commun.* **2011**, *47*, 8210.

[120] H. W. Horn, G. O. Jones, D. S. Wei, K. Fukushima, J. M. Lecuyer, D. J. Coady, J. L. Hedrick, J. E. Rice, *J. Phys. Chem. A.* **2012**, *116*, 12389.

[121] F. Liu, Z. Li, S. Yu, X. Cui, X. Ge, *J. Hazard. Mater.* **2010**, *174*, 872.

[122] F. Liu, L. Li, S. Yu, Z. Lv, X. Ge, *J. Hazard. Mater.* **2011**, *189*, 249.

[123] M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, S. Yu, *ACS Sustain. Chem. Eng.* **2018**, *6*, 13114.

[124] F. Liu, J. Guo, P. Zhao, M. Jia, M. Liu, J. Gao, *Polym. Degrad. Stab.* **2019**, *169*, 108996.

[125] J. Guo, M. Liu, Y. Gu, Y. Wang, J. Gao, F. Liu, *Ind. Eng. Chem. Res.* **2018**, *57*, 10915.

[126] X. Song, W. Hu, W. Huang, H. Wang, S. Yan, S. Yu, F. Liu, *Chem. Eng. J.* **2020**, *388*, 124324.

[127] W. Huang, H. Wang, W. Hu, D. Yang, S. Yu, F. Liu, X. Song, *RSC Adv.* **2021**, *11*, 1595.

[128] C. Alberti, S. Enthaler, *Asian J. Org. Chem* **2020**, *9*, 359.

[129] C. Alberti, F. Scheliga, S. Enthaler, *Chemistry Open* **2019**, *8*, 822.

[130] Y. Zhao, X. Zhang, X. Song, F. Liu, *Catal. Lett.* **2017**, *147*, 2940.

[131] T. Yang, C. Wang, F. Liu, X. Sun, G. Qin, Y. Liu, J. Gao, *J. Mater. Sci.* **2019**, *54*, 9442.

[132] Y.-Y. Liu, G.-H. Qin, X.-Y. Song, J.-W. Ding, F.-S. Liu, S.-T. Yu, X.-P. Ge, *J. Taiwan Inst. Chem. Eng.* **2018**, *86*, 222.

[133] Y. Zhao, H. Jiang, S. Xue, M. Liu, F. Liu, S. Yu, *Solid State Sci.* **2020**, *107*, 106317.

[134] F. Liu, Y. Xiao, X. Sun, G. Qin, X. Song, Y. Liu, *Chem. Eng. J.* **2019**, *369*, 205.

[135] W. Huang, H. Wang, X. Zhu, D. Yang, S. Yu, F. Liu, X. Song, *Appl. Clay Sci.* **2021**, *202*, 105986.

[136] D. Kim, B. K. Kim, Y. Cho, M. Han, B. S. Kim, *Ind. Eng. Chem. Res.* **2009**, *48*, 685.

[137] A. Oku, S. Tanaka, S. Hata, *Polymer* **2000**, *41*, 6749.

[138] C. H. Lin, H. Y. Lin, W. Z. Liao, S. A. Dai, *Green Chem.* **2007**, *9*, 38.

[139] D. Pant, *Process Saf. Environ. Prot.* **2016**, *100*, 281.

[140] K. Hidaka, Y. Iwakawa, T. Maoka, F. Tanimoto, A. Oku, *J. Mater. Cycles Waste Manag.* **2009**, *11*, 6.

[141] C. Jehanno, J. Demarteau, D. Mantione, M. C. Arno, F. Ruipérez, J. L. Hedrick, A. P. Dove, H. Sardon, *ACS Macro Lett.* **2020**, *9*, 443.

[142] Y. Zheng, J. Xu, *J. Prog. Chem.* **2014**, *26*, 1471.

[143] K. Saito, C. Jehanno, L. Meabe, J. L. Olmedo-Martínez, D. Mecerreyes, K. Fukushima, H. Sardon, *J. Mater. Chem. A* **2020**, *8*, 13921.

[144] S. Hata, H. Goto, E. Yamada, A. Oku, *Polymer* **2002**, *43*, 2109.

[145] S. Hata, H. Goto, S. Tanaka, A. Oku, *J. Appl. Polym. Sci.* **2003**, *90*, 2959.

[146] C. G. Kim, M. J. Son, J. Y. Do, *Eur. Polym. J.* **2021**, *156*, 110611.

[147] H. Zhou, R. Zhang, H. Zhang, S. Mu, X. B. Lu, *Sci. Technol.* **2019**, *9*, 1457.