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Catalyst residues severely impact the thermal stability and degradation mechanism of polycarbonates: How to turn a flaw into an opportunity

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ABSTRACT

Three poly(cyclohexene carbonates) with molecular weights ranging from 4.9 to 9.4 kg/mol were synthesized from cyclohexene oxide and CO_2 using macrocyclic phenolate dimetallic catalysts and purified by conventional purification procedure. A decrease in thermal stability of approximately 100 °C was observed in comparison to poly(cyclohexene carbonates) with similar molecular weights synthesized using salen metal catalysts. This decrease derives from the presence of traces of dimetallic catalyst which is able to promote the depolymerisation of poly(cyclohexene carbonate) to CO_2 and cyclohexene oxide in contrast to the usual backbiting mechanism that leads to cyclic carbonate. The onset of the degradation can be precisely tuned by changing the amount of residual dimetallic catalyst or including species with functional groups that can reduce the availability of the catalytic centers. Therefore, the possibility of controlling the thermal stability of poly(cyclohexene carbonates) by varying the concentration of the catalyst and the surrounding chemical environment paves the way for the use of these polymers as components in self-sacrificial materials of interest for advanced applications.

1. Introduction

Carbon dioxide (CO_2) has nowadays received increasing interest as raw material for chemical synthesis due to its abundance, cheapness and low toxicity, in addition to the beneficial effects of storing a greenhouse gas. Currently, several processes including CO_2 as a main reactant have been reported for the synthesis of fine chemicals and polymers [1,2]. Among these, the production of aliphatic polycarbonates from CO_2 and epoxides was widely investigated since Inoue's seminal work in 1969 [3–6], in which polypropylene carbonate (PPC) was obtained from propylene oxide and CO_2 using $ZnEt_2/H_2O$ heterogeneous catalyst [7]. Due to the high chemical inertness of CO_2, appropriate catalysts are necessary to bring about the epoxide/CO_2 alternating copolymerization. Both heterogeneous and homogeneous catalysts have been described in the last 30 years, with better performances for the latter [6]. Typical examples of heterogeneous catalysts [8–13] are those based on zinc glutarates, zinc adipate and rare-earth whereas homogeneous systems

generally consist of one or more metallic ions coordinated by organic ligands. The first generation of catalysts, such as aluminium porphyrin [14], zinc phenoxide [15] and zinc β-diiminate [16–18] complexes, are now replaced by salen metal catalysts and macrocyclic phenolate dimetallic catalysts, introduced by Darensbourg [19] and Williams [20], respectively. The structure of a typical salen metal catalyst containing a chrome (Cr) central cation is reported in Fig. 1 (cat. 1) [21] where the X ligand is an anionic species such as Cl⁻, N₃⁻, Br⁻, I⁻ or AcO⁻ (acetate group) [19]. Other metals as cobalt (Co) [22] and aluminium (Al) [23] were also investigated. The efficiency of salen metal catalysts strongly depends on additional species with the role of cocatalysts. Typical cocatalysts are neutral nucleophiles such as 4-dimethylaminopyridine (DMAP) or soluble "onium" salts such as PPNX, in which PPN⁺ is the bis (triphenylphosphine)iminium cation and X⁻ could be a Cl⁻, N₃⁻, AcO⁻ or 2,4 dinitrophenolate anions [24,25,26]. Recently, novel quaternary phosphonium salts such as tetra-phenylphosphonium chloride (TPPCl), triphenyl(4-pyridinylmethyl)-phosphonium chloride hydrochloride

(UHFFA) and branched phosphazenium salts (*i.e.* tetrakis[tris(dimethylamino) phosphoranylideneamino] phosphonium chloride or azide) have been reported as effective cocatalysts alternative to PPNX salts [27,28,29]. Reaction temperatures are generally set between 50 and 100 °C with CO_2 pressure ranging from 10 to 55 bar [30]. Considerably lower pressures are generally sufficient when macrocyclic phenolate dimetallic catalysts are used [20]. In these cases, a CO_2 loading of 1 bar is commonly reported [6]. As a typical example, a system where both metal centres are magnesium (Mg) [31] cations is reported in Fig. 1 (cat. 2). Catalysts with zinc (Zn) [20,32–34], cobalt (Co) [35] and iron (Fe) [36] metal centres were also reported. Such complexes may present at the two central positions both the same metal or different metals, with a remarkable activity for the latter [37,38]. Typical X ligands are anions like AcO^-, CF_3COO^- (trifluoroacetate group) and Br^- [31,39,40].

The catalysts described above have been used to copolymerize CO_2 with a huge number of epoxides [41–43], but certainly the two most commonly investigated are propylene oxide (PO) and cyclohexene oxide (CHO) leading to polypropylene carbonate (PPC) and poly(cyclohexene carbonate) (PCHC), respectively. PPC is a high-toughness amorphous polymer with a relatively low glass transition temperature ($T_g < 45$ °C), low modulus and yield strength of ~30 MPa. The combination of these characteristics precludes the application of PPC as both engineering material and elastomer [6,44,45]. On the contrary, PCHC is a brittle material with T_g slightly higher than 100 °C and tensile modulus of ~2.5 GPa [6], thus suggesting a polystyrene-like behavior with potential applications as hard plastic. Moreover, the mechanical properties of PCHC can be further enhanced by synthesizing highly stereoregular samples with pseudo-crystalline structure and melting temperature of 272 °C [46–48]. Unfortunately, PCHC is hard to be processed due to its relatively low degradation temperature. In fact, the 5 % and 50 % weight loss temperatures ($T_{5\%}$ and $T_{50\%}$) of PCHC measured by thermogravimetric analyses are ~285 and 305 °C respectively, thus indicating a thermal stability lower than the commercial bisphenol A-derived polycarbonate, which presents a $T_{50\%}$ of 460 °C [44,49,50]. Interestingly, stereoregularity and crystallinity do not significantly influence the thermal degradation of the polymer [48].

In this context, detailed studies have been carried out to elucidate the degradation mechanism of PCHC, with the explicit target of increasing its thermal stability. Pyrolysis-gas chromatography-mass spectrometry experiments demonstrated that the most relevant degradation process occurring at 250 °C is a backbiting reaction initiated by the hydroxyl end-group of PCHCs (Fig. 2, path a). Cyclic carbonate is the principal by-product [51]. Random scission of the polymer chain becomes competitive with the backbiting reaction at temperatures higher than 400 °C and the evolution of different degradation products such as cyclic alkenes was observed. Partial inhibition of the backbiting process was obtained

by capping the hydroxyl end-groups of PCHC with maleic anhydride, thus resulting in a degradation temperature increase of more than 20 °C [52]. In this respect, several species such as maleic anhydride and benzoyl chloride were used as capping agents to stabilize PPC by preventing the onset of the backbiting [53,54] process. A further increase in the thermal stability of aliphatic polycarbonates was obtained by copolymerizing epoxides and CO_2 with monomers such as caprolactone or by adding inorganic fillers to the polymer matrix. For example, layered zinc phenylphosphonate and modified graphite oxide were demonstrated to thermally stabilize PCHC and PPC respectively [55,56]. On the contrary, the presence of residual catalyst is strongly detrimental for the thermal stability of the samples [57]. For example, a 56 °C decrease [58] in degradation temperature was noted in PCHCs prepared using a Zn-containing catalyst due to the presence of some residual traces of catalyst. Interestingly, some authors highlighted how the introduction of specific catalysts inside a product can be of advantage in terms of chemical recycling of the material [59,60]. For example, Liu et al. demonstrated that PCHC containing 0.2 mol% of salen-chromium catalyst and bis(triphenylphosphine)iminium-based cocatalyst completely depolymerizes to produce CHO and CO_2 in solid state conditions at 200 °C [61].

Recently, Williams et al. carried out a complete depolymerization of PCHC to CHO and CO_2 in bulk using macrocyclic phenolate dimetallic catalysts containing Mg/Mg or Mg/Co central ions (catalyst loading lower than 0.3 mol%) [62,63]. This alternative degradation path mediated by catalysts is described in Fig. 2 (path b). In this perspective, epoxides and CO_2 may be polymerized and depolymerized several times in a perfect frame of circular economy.

In the present work, a detailed study of the thermal stabilities of PCHCs synthesized by macrocyclic phenolate dimetallic catalysts is carried out in comparison to PCHC samples obtained with traditional salen metal catalysts. The role of residual traces of catalyst remaining in samples after purification by conventional procedures was highlighted. Finally, the depolymerizing effect of the catalysts is evaluated in polymer blends even in the presence of functional polymers to further clarify the effect of the media conditions on the onset and nature of the degradation process.

2. Results and discussion

Three PCHCs were prepared using the salen metal catalyst (cat. 1, Fig. 1) in combination with different cocatalysts as indicated in Table 1. The samples are referred to as PCHC-1(M_n), with M_n being the average molecular weight of the polymer. Preparation and material characterization were reported elsewhere [27].

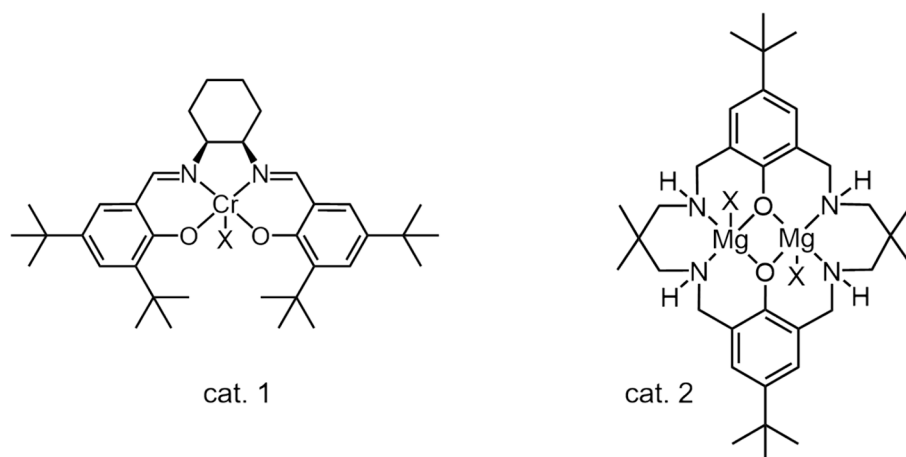Furthermore, three PCHC samples were synthesized using cat. 2

Fig. 1. Salen metal catalyst with Cr ion as the metal centre (**cat. 1**) and macrocyclic phenolate dimetallic catalyst with two central Mg ions (**cat. 2**).
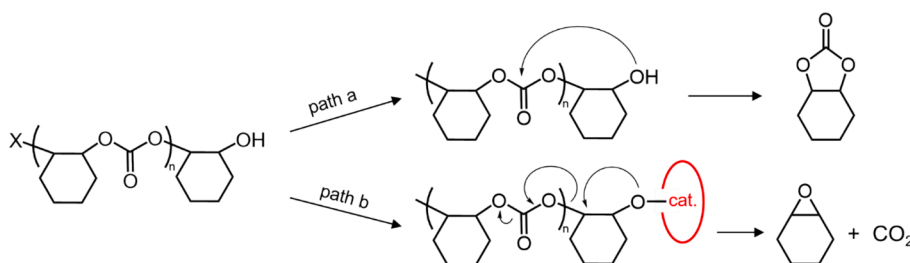
Fig. 2. Degradation paths of PCHC: backbiting reaction (path a) and catalyst mediated depolymerisation reaction (path b).

Table 1

Catalyst, cocatalyst and catalyst-associated X ligand employed in the synthesis of PCHC samples. The average molecular weight (M_n), the dispersity index (Đ), the glass transition temperature (T_g), the 5 % and 50 % weight loss temperatures ($T_{5\%}$ and $T_{50\%}$) of each polymer are also included.

Sample	Catalyst	Cocatalyst	X	M_n (kg/mol)	Đ	T_g (°C)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
PCHC-1(9.2)[a]	cat.1	TPPCl	Cl⁻	9.2	1.10	108	260	281
PCHC-1(7.6)[a]	cat.1	DMAP	Cl⁻	7.6	1.20	100	256	273
PCHC-1(9.1)[a]	cat.1	UHFFA	N₃⁻	9.1	1.10	111	263	294
PCHC-2(9.4)[b]	cat.2	–	AcO⁻	9.4	1.27	108	148	168
PCHC-2(4.9)[b]	cat.2	–	Br⁻	4.9	1.25	103	162	189
PCHC-2(5.4)[b]	cat.2	–	Br⁻	5.4	1.22	98	145	164

[a] Reactions carried out at 80 °C for 3.5 h at the pressure of 30 bar.

[b] Reactions carried out at 80 °C for 24 h at the pressure of 4 bar.

(Fig. 1) with X being AcO⁻ or Br⁻ as reported in Table 1. All the reactions were carried out at 80 °C and 4 bar for 24 h. Then, the chain growth was stopped by adding to the reaction vessel 5 mL of dichloromethane and 0.2 mL of a hydrochloric acid solution (5 % in weight) in methanol. The polymer samples were then purified by two sequential precipitations in cold methanol from dichloromethane solutions and dried under vacuum [27,31]. The average molecular weight and the dispersity index (Đ) of these samples, henceforth marked as PCHC-2(M_n), were determined by size exclusion chromatography (SEC). The obtained chromatograms are reported in Fig. 3a while M_n and Đ values are collected in Table 1. Significantly lower molecular weights were obtained when X = Br⁻, thus indicating the occurrence of chain transfer processes promoted by water traces, as widely reported in literature [31].

Both PCHC-1 and PCHC-2 samples were characterized by ¹H NMR and ¹³C NMR spectroscopy and full spectra are reported in the Supporting Information.

¹H NMR spectra confirm the alternation of CO₂ and epoxides in all

samples without significant presence of ether bonds. Furthermore, a careful assignment of the signals shows that polymers contain at least one hydroxy end-group. These groups derive either from the protonation of the growing chains at the end of the reaction or from chain transfer processes taking place during the synthesis. These data are in good agreement with literature [27].

The polymer tacticity was evaluated by ¹³C NMR spectra analysis according to the method described in literature [64–66]. Fig. 3b reports the comparison between the normalized carbonyl signals of PCHC-1 (9.2) and PCHC-2(5.4) together with the picture of the stereochemical structures associated to each signal. The signal at 153.8 ppm is associated to carbonyl groups contained in RR-RR (SS-SS) sequences whereas the signals of SS-RR (RR-SS) sequences are comprised between 153.1 and 153.3 ppm. Accordingly, the simultaneous presence of both signals at 153.8 ppm and 153.1–153.3 ppm indicates that both samples are atactic. However, the signal at 153.8 ppm is always more intense for samples PCHC-1 than PCHC-2 thus revealing that polycarbonates PCHC-
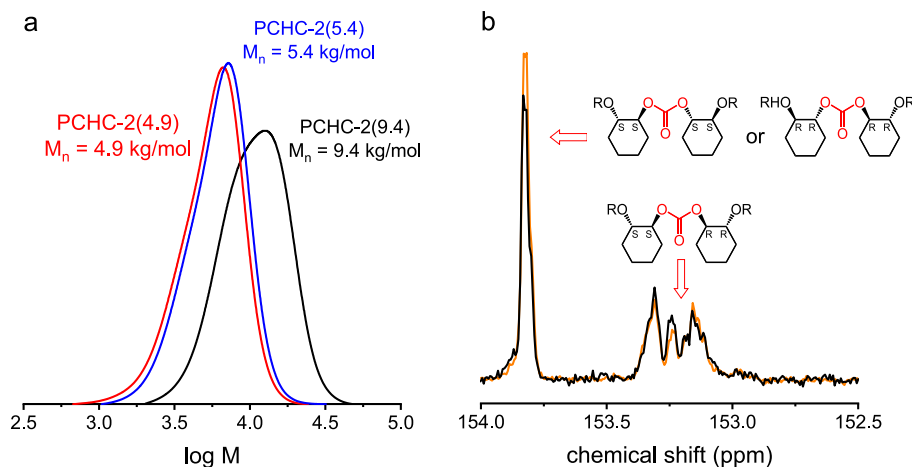

Fig. 3. (a) SEC chromatograms of the PCHC-2(9.4), PCHC-2(4.9) and PCHC-2(5.4) samples. (b) ¹³C NMR spectra of the PCHC-1(9.2) and PCHC-2(5.4) samples (zoom in the 152.2–154.0 ppm range). Chemical structures of the sequence associated to the ¹³C NMR signals are also included.

1 and PCHC-2 slightly differ in sequence content. The percentage of SS-SS (RR-RR) sequences is estimated 55 % ($\pm$2) for PCHC-1 samples and decreases to 49 % ($\pm$1) for PCHC-2.

MALDI-TOF analysis of PCHC-1 samples was already described [27]. Two polymer species were observed, differing in the chemical nature of the end-groups. In detail, polycarbonates characterized by a chlorine atom at one end and a hydroxyl group on the other one were observed as expected according to the polymerization mechanism. In addition, polycarbonates characterized by hydroxy groups at both chain ends were also present as deriving from chain transfer processes promoted by water traces [31]. MALDI-TOF analysis was also performed for PCHC-2 samples and full spectra are reported in the Supporting Information. Polycarbonates that are hydroxy-terminated on both the chain ends are present also in PCHC-2 samples, thus confirming the occurrence of transfer processes during the synthesis. Furthermore, bromine end groups were identified in samples PCHC-2(4.9) and PCHC-2(5.4) whereas acetate end group is observed in sample PCHC-2(9.4).

Glass transition temperatures of PCHC-1 and PCHC-2 samples were determined by Differential Scanning Calorimetry (DSC) and are included in Table 1 whereas Fig. 4a reports the corresponding DSC heating traces. T_g values range from 98 to 111 °C in agreement with literature [44,67]. In this respect, no significant differences between PCHC-1 and PCHC-2 samples can be noticed.

A completely different scenario is observed when thermogravimetric analysis (TGA) is performed. Fig. 4b reports the relevant TGA curves under nitrogen whereas $T_{5\%}$ and $T_{50\%}$ values for PCHC-1 and PCHC-2 samples are included in Table 1. $T_{5\%}$ and $T_{50\%}$ of PCHC-1 samples are approximately 260 and 283 °C in good agreement with literature data [44]. In contrast, $T_{5\%}$ and $T_{50\%}$ of PCHC-2 are 152 and 174 °C with a drop of more than 100 °C. Considering the similarity of PCHC-1 and PCHC-2 samples in molecular weight and tacticity and reasoning that the terminal group nature does not seem to influence the degradation of the samples, since bromine and acetate terminated polycarbonates show exactly the same $T_{5\%}$ and $T_{50\%}$, such a huge difference in thermal stability suggests the presence of some degradation-promoting impurities in PCHC-2 polymers.

A more detailed picture was obtained by evaluating the products that evolve during the thermal degradation using the Direct Exposure Probe (DEP) technique [68,69]. A thin film of the investigated sample is deposited onto a filament and then annealed with a heating ramp of 60 °C/min from 25 to 400 °C directly in a mass spectrometer where the degradation products that evolve during heating are analyzed. **Figure SI16** (Supporting Information) reports a comparison between TGA and full scan DEP data (in the integral and derivative forms) of samples PCHC-1(9.2) and PCHC-2(9.4). TGA and DEP curves present a

similar shape with the DEP ones translated towards higher temperature because of the higher heating rate [70]. As it is possible to extract fragments with specific *m/z* values from full scan data, the DEP analysis is able to provide information about the degradation mechanism. Fig. 5 reports the signals of the most intense molecular fragments for PCHC-1
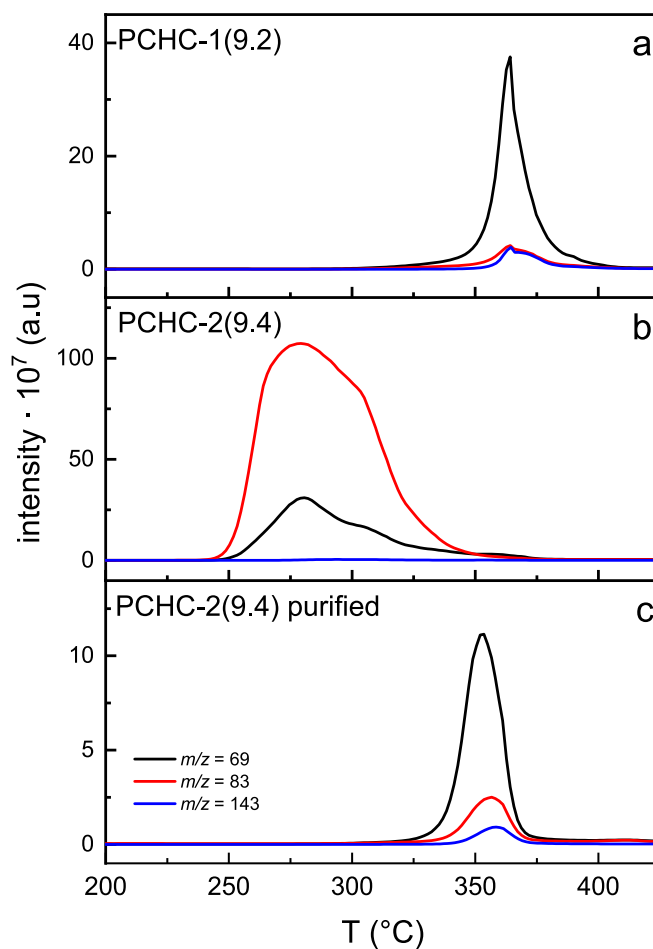
Fig. 5. DEP analyses carried out on the PCHC-1(9.2) (a), PCHC-2(9.4) (b) and PCHC-2(9.4) purified by SEC (c) samples. The evolution of the fragments with *m/z* of 69, 83 and 143 is reported as a function of the temperature. The samples were subjected to a heating ramp of 60 °C/min.
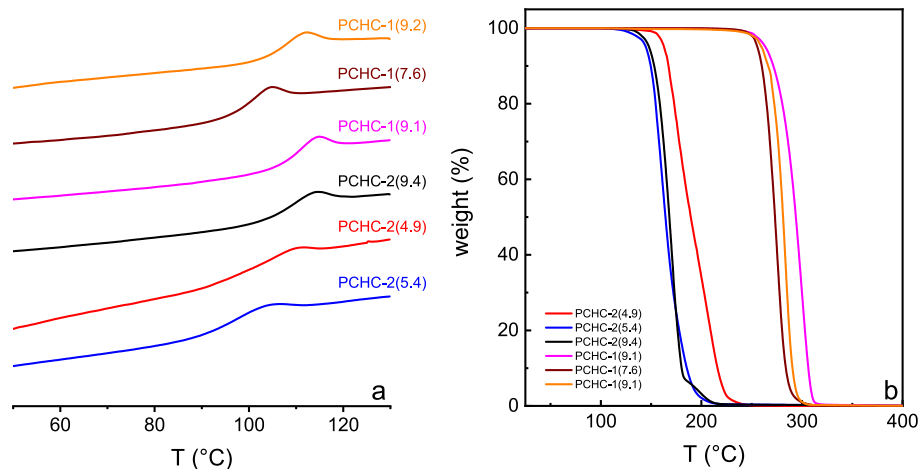
Fig. 4. **(a)** Second run DSC thermograms of PCHC-1 and PCHC-2 samples. **(b)** TGA curves of the PCHC-1 and PCHC-2 samples. Both analyses were carried out under nitrogen atmosphere with a heating ramp of 10 °C/min.

(9.2) and PCHC-2(9.4) as a function of temperature in the derivative form. Once subjected to the above thermal treatment, PCHC-1(9.2) begins to degrade at 330 °C and reaches the maximum evolution rate at approximately 360 °C. The main fragments present mass per charge (m/z) values of 143, 83 and 69. The presence of these fragments and its relative intensities suggest cyclohexene carbonate (CHC) as the principal degradation product (the fragment at 143 is the molecular ion of CHC). Therefore, the principal degradation path for PCHC-1 is consistent a backbiting mechanism (Fig. 2, path a). In contrast, once subjected to the same thermal treatment, PCHC-2(9.4) begins to degrade at 240 °C and reaches the maximum evolution rate at less than 300 °C, mainly releasing the fragments at m/z of 83 and 69. No traces of the molecular ion of CHC was observed and the relative intensities of fragments 83 and 69 suggest CHO as the principal degradation product. Therefore, PCHC-2 samples degrade according to the catalyst-mediated degradation mechanism of path b in Fig. 2.

The impressive difference in the thermal stability and degradation mechanism for nearly identical polymers suggests the action of an external component such as for example a catalyst residual trace in PCHC-2 samples at a concentration not detectable by NMR spectroscopy. To confirm this hypothesis, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analyses, performed on PCHC-2(9.4) was carried out and revealed the presence of magnesium in quantities of 170 ± 15 μg/g.

Assuming that cat. 2 is intact and therefore all the magnesium determined by ICP-AES is incorporated in the catalyst, the above data indicates the presence of one molecule of cat. 2 for every ~2000 cyclohexene carbonate repeating units. Such a low amount is indeed well below the NMR detection limit. Degradation processes mediated by dimetallic catalysts such as cat. 2 were already reported for catalyst-on-repeating unit molar ratios in bulk ranging from 300 to 10,000 [63]. Moreover, it is interesting to observe that approximately 25 % of the catalyst loaded into the reaction vessel remains in the polymer after the purification step. Therefore, the adopted work out procedure is unable to fully purify the polymeric product. Considering the molecular weight of the sample PCHC-2(9.4) and assuming that all chains have one hydroxyl end-group (the role of water as transfer agent during the synthesis is neglected so the number of hydroxy groups is underestimated), it is expected the occurrence of one cat. 2 molecule every 30 hydroxy end groups. Such an excess of hydroxy groups could justify the strong tendency of the catalyst to be retained by the polymeric material during the purification steps because of the establishment of specific interactions.

An effective purification procedure for PCHC-2(9.4) sample was carried out by preparative SEC using THF as the solvent and collecting only the portion of eluent containing the polymer (the full chromatogram is reported in **Figure SI18** with the sampling time highlighted). The separated sample was then dried and analyzed by DEP. The sample displays a remarkably increase in the thermal stability and the evolution of the degradation fragments, reported in Fig. 5c, is very similar to that of PCHC-1(9.2) indicating the occurrence of the backbiting degradation mechanism.

In principle, controlled catalyst additions within PCHC could be the key to the chemical recycling in a sustainable economy perspective [62,63] and, conversely, to be processed by conventional manufacturing techniques, PCHC-based materials should be free from any trace of catalyst. However, completely reversing the point of view, polycarbonates containing small amounts of catalyst could be considered as self-sacrificial materials [71] with several potential applications as for example in microelectronic processes where controlled degradation/depolymerization steps are involved. In this perspective, the catalyst in the polycarbonate represents a trigger modulator of the thermally activated depolymerization. Typical processes in which the use of polymers with tuned degradation can be of benefit are the polymer doping of silicon substrates [72,68,73,74,75] and the preparation of nanolithographic masks [76,77]. Therefore, some experiments were performed to establish the performance characteristics of the residual catalyst in directing and tuning the PCHC thermal degradation process. In details, PCHC-2(9.4) sample was mixed, in solution with different weight percentages ranging from 90 to 1 %, with PCHC-1(9.2) (prepared using the salen catalyst and therefore without traces of the dimetallic catalyst). Several binary blends were obtained in which the amount of PCHC-1 (9.2) tunes the amount of cat. 2. In particular, the molar ratio between cyclohexene carbonate repeating units and cat. 2 increases from 2000 to 200,000 reaching catalyst concentrations lower than the limit explored so far [63]. The thermal degradation of the blends was investigated by DEP analyses. Full scan data in the integral form are reported in Fig. 6a whereas the derivative representation of full scan is included in Supporting Information (see **Figure SI19**). Moreover, the prevalence of backbiting reaction over the catalyst mediated depolymerisation reaction was accounted for by evaluating the ratio (R) between the signal areas of the evolved fragments at m/z 143 and 83 relevant to the backbiting and catalyst-mediated degradation path, respectively (Fig. 6b). The thermal degradation profile of blends containing less than 10 % PCHC-2(9.4) is very similar. In contrast, on further increasing the amount of PCHC-2(9.4), the degradation temperature decreases due to the progressive concentration of the catalyst in the blend. Furthermore, depolymerization is the main degradation path in all the blends up to 30 % of PCHC-2(9.4). A significant amount of fragment at $m/z = 143$ was observed for blend with 10 % of PCHC-2(9.4), leading to an R value of 0.11, thus indicating the occurrence of some backbiting process in parallel to depolymerization. The incidence of the backbiting process increases on further decreasing the PCHC-2(9.4) percentage. The results just discussed and the literature data [63] indicate that when PCHCs contain more than one catalyst molecule every ~10,000 the polycarbonate degrades to epoxides and CO_2, whereas for lower concentrations the backbiting mechanism begins to play a significant role.

In order to expand the case studies considered, PCHC-2(9.4) sample was also blended with two polystyrene samples PS and PSOH with similar molecular weight but different end-groups (Table 2). PS is a commercial polymer prepared by anionic polymerization and presents the typical saturated end group whereas PSOH was prepared by ARGET ATRP and presents a bromine atom and a hydroxy group at the end.

To exclude the contribution of the polystyrene degradation, leading to styrene and oligomers, DEP analysis was carried out in SIM (single ion monitoring) mode considering only the fragments at m/z 143 and 83. SIM data in integral form are reported in Fig. 7a and b for blends of PCHC-2(9.4) with PSOH and PS respectively, whereas Fig. 7c reports the trend of R for both blend series as a function of the PCHC-2(9.4) in the blend. Finally, Fig. 7d describes the trend of the degradation temperature relevant to 50 % weight loss of the polycarbonate component in the blends. For comparison purposes, Fig. 7d reports also the degradation temperature relevant to 50 % weight loss of the blends between PCHC-2 (9.4) and PCHC-1(9.2).

Apparently, the trend of the degradation for blends between PCHC-2 (9.4) and PSOH or PS is very similar. However, R is close to zero for each composition of the blend with PS whereas an increase in R is observed when PSOH is employed at percentages higher than 50 %, thus indicating a switch from depolymerization to backbiting degradation mechanism. In particular, R approaches the limit value of 0.64 when the PSOH percentage is 90 %. If we assume that the coordination efficiency of the hydroxy groups relevant to PSOH is equal to the one of PCHC-2 (9.4), in the 70 % PSOH blend it is possible to estimate ~50 extra hydroxyl end-groups for each residual cat. 2 molecules and such number increases to ~200 when the percentage of PSOH is 90 %. These results suggest the occurrence of interactions between the hydroxyl end-groups of PSOH and cat. 2 and a consequent decrease of the availability of the active centers.

3. Conclusions

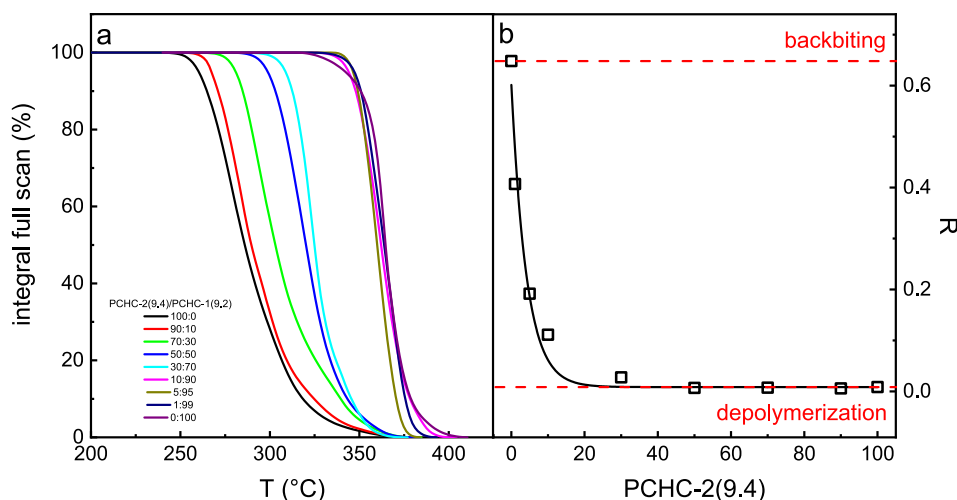Three poly(cyclohexene carbonates) with molecular weights ranging

Fig. 6. Degradation of the blend containing PCHC-2(9.4) and PCHC-1(9.2) as a function of the annealing temperature. The degradation profiles were obtained by plotting in the integral form the full scan data from the DEP analyses.

Table 2
The average molecular weight (M_n), the dispersity index and the end-groups of PS and PSOH.

Sample	M_n (kg/mol)	Đ	End groups
PSOH	13	1.09	OH, Br
PS	10	1.06	CH_3, H

from 4.9 to 9.4 kg/mol were synthesized from cyclohexene oxide and CO_2 using macrocyclic phenolate dimetallic catalysts and purified by conventional purification procedure. Chemical structure, tacticity and thermal properties of these polymers were analyzed and compared with those of three reference poly(cyclohexene carbonates) with similar molecular weight synthesized using salen metal catalysts. A decrease in thermal stability of approximately 100 °C was observed in the samples synthesized with dimetallic catalysts, although no significant structural differences were found between these samples and the reference ones. This decrease in thermal stability was found to derive from the presence of traces of the dimetallic catalyst which is able to promote the depolymerisation of poly(cyclohexene carbonate) to CO_2 and cyclohexene oxide. The complete removal of these traces by size exclusion chromatography results in samples having thermal stability comparable to that of the reference polycarbonates thus suggesting that conventional catalyst removal methods are not efficient to fully purify the products. Furthermore, by preparing and studying suitable blends, it was demonstrated that the onset of degradation and the nature of the evolved species can be precisely tuned by changing the amount of residual catalyst contained in the PCHC or by including species with functional groups that can reduce the availability of the catalytic sites. In this line, the possibility of controlling the thermal stability of poly(cyclohexene carbonates) by varying the concentration of the residual catalyst and the surrounding chemical environment paves the way for the use of these polymers as self-immolative materials of interest for advanced applications.

4. Experimental section

Materials. All chemicals were purchased by Merck and used as received except for cyclohexene oxide (CHO) which was dried on calcium hydride before use. The catalyst (cat. 2) was synthesized in accordance with the procedure described in literature [31]. The synthesis of the three poly(cyclohexene carbonate) samples PCHC-1(9.2), PCHC-1(7.6) and PCHC-1(9.1) were previously reported [27]. The polystyrene PS was purchased by Merck and used as received.

Synthesis of poly(cyclohexene carbonates) with cat. 2. Three samples PCHC-2(9.4), PCHC-2(4.9) and PCHC-2(5.4) were synthesized following the same procedure. 5 mL of CHO (0.05 mol) and 36 mg of cat. 2 (0.05 mmol) were added in a Buchi Miniclave pressure reactor under inert atmosphere in a MBRAUN LABstar glove box. The reactor was filled with CO_2 at a constant pressure of 4 bar and the reaction was carried out at 80 °C for 24 h under magnetic stirring. The reaction mixture was then dissolved in 5 mL of dichloromethane and 0.2 mL of a hydrochloric acid/methanol solution 5 % by weight was added. The solution was concentrated in a rotavapor and dropped into cold methanol to precipitate the polymer. The polymer was dried under vacuum, precipitated a second time in cold methanol from fresh dichloromethane and dried again. Monomer conversions were estimated gravimetrically and result approximately 50 %.

Synthesis of the hydroxyl-terminated polystyrene PSOH. PSOH was synthesized by Activators ReGenerated by Electron Transfer-Atom Transfer Radical Polymerization (ARGET-ATRP) as reported in literature [72]. In detail, 1.9 mg (8.52 μmol) of copper (II) bromide ($CuBr_2$), 2.3 μL (8.62 μmol) of tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and 63 μL (0.43 mmol) of 2-hydroxyethyl(2-bromoisobutyrate) (HEBIB) were dissolved in 5 mL of anisole and 10 mL of styrene (87.11 mmol) in a Schlenk flask and the mixture was degassed by two freeze–thaw cycles. A solution of 35.2 mg (86.91 μmol) of tin (II) 2-ethylhexanoate (Sn(EH_2)) and 23.2 μL (86.91 μmol) of Me_6TREN in 1 mL of anisole was then added and the mixture was degassed again by another freeze–thaw cycle. The flask was introduced in an oil bath and the synthesis was carried out at 90 °C for 22 h. The polymer was then collected and purified through two precipitations in cold methanol from THF.

Polymer characterization. Molecular weights and dispersity indexes of the samples were evaluated by SEC using a 590 Waters chromatograph equipped with Waters HSPgel HR3 and HR4 columns and a refractive index detector. The column temperature was set at 25 °C. The analyses were carried out using THF as the eluent at the flow rate of 0.3 mL/min. The calibration was performed by using standard polystyrenes with molecular weight ranging from 1 to 100 kg/mol.

^{1}H NMR and ^{13}C NMR spectra were collected from deuterated-chloroform solutions at room temperature using a liquid-state Bruker instrument (500 MHz).

MALDI-TOF analysis were performed in linear mode with an UltrafleXtreme instrument. The accelerating voltage and the delay time were set to 20 kV and 250 ns, respectively, and 1000 laser shots were collected for each sample. Deflection up to 2000 *m/z* was used to suppress the matrix signals. The samples were prepared by put on the sample plate a single drop of a solution prepared by mixing the matrix
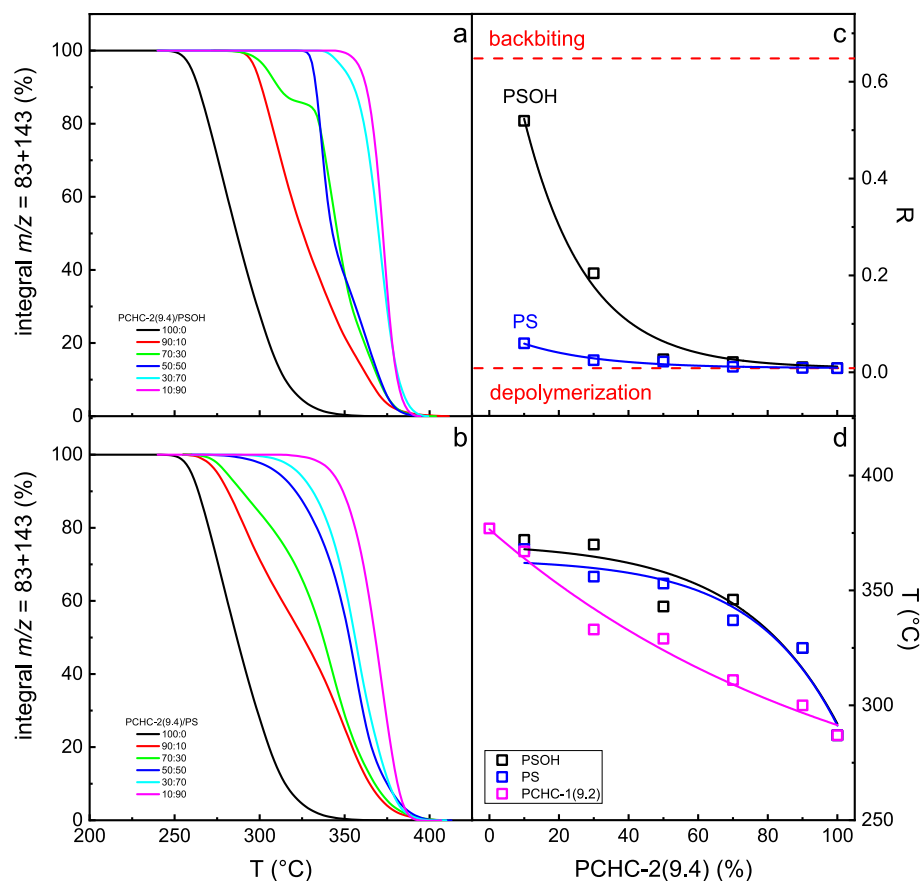
Fig. 7. Degradation of PCHC-2(9.4) blended with PSOH (a) and PS (b) as a function of the annealing temperature. The degradation profiles were obtained by DEP data collected considering the sum of the fragments with m/z of 83 and 143 and reported in the integral form. Ratio (R) between the signal areas relative to the fragments with m/z of 143 and 83 evolved during the DEP analyses carried out on polymer blends of PCHC-2(9.4) and PS or PSOH as a function of PCHC-2(9.4) weight percentages (c). Degradation temperature relevant to 50% weight loss of PCHC-2(9.4) in the blends with PS or PSOH. For comparison, also the degradation temperature relevant to 50% weight loss of the blends between PCHC-2(9.4) and PCHC-1(9.2) is included.

solution (20 mg of DCTB in 1 mL of THF), the polymer solution (10 mg of polycarbonate in 1 mL of THF) and the salt solution (0.1 M of NaTFA in THF) in a volume ratio of 25/5/2.

DSC analyses were performed by a Mettler-Toledo Calorimetry mod. 821e. 5 mg of each sample was placed in an alumina-sealed crucible and heated from 25 to 130 °C at a heating rate of 20 °C/min, cooled to 50 °C at 10 °C/min and heated again to 130 °C at 10 °C/min. The second heating was considered to estimate the T_g of the sample.

TGA were performed by a Mettler-Toledo TGA/SDC 3+ instrument under nitrogen flow from 25 to 400 °C at a heating rate of 10 °C/min.

Polymer purification. PCHC-2(9.4) sample was purified from catalyst residues using a preparative liquid chromatograph (thermo scientific UltiMate 3000) equipped with an injection loop of 300 μL, a Waters HSPgel HR3 column and a refractive index detector·THF was used as the eluent at the flow rate of 0.3 mL/min. The fraction of eluted solution containing the polymer was collected, dried and analyzed by DEP analyses.

Polymer blend preparation. Solutions consisting of 10 mg of PCHC-2 (9.4), PCHC-1(9.2), PS and PSOH in 2 mL of dichloromethane were prepared and stirred for 24 h. Appropriate volumes of PCHC-2(9.4) were mixed with those of the other polymer making the blend. Moreover, fresh dichloromethane was added to obtain in all cases a 1 mg/mL solution with the desired blend composition. Such mixtures were stirred again for 2 h and then employed in DEP analyses.

DEP analyses. The analyses were performed using a Direct Exposure Probe hyphenated with a single quadrupole mass spectrometer (Thermo Scientific ISQ LT). A 3 μL drop of a polymer solution (1 mg/mL of dichloromethane) was deposited on the rhenium filament on the top of

the probe and the solvent was eliminated by heating the filament at 50 °C for 1 min. After that, the probe was inserted directly in the spectrometer and the sample was annealed from 25 to 600 °C at a heating rate of 60 °C/min. The molecular fragments produced by the degradation of the polymer deposited on the probe filament are then collected and analyzed in the mass spectrometer. The analyses were performed in the EI + mode with the ionization energy of 70 eV. The signal was acquired both in full scan mode, where all fragments with m/z from 45 to 300 were collected, and in Single Ion Monitoring (SIM) mode, in which only fragments with m/z = 69, 83 and 143, typical of the poly(cyclohexene carbonate) degradation, and 104, typical of styrene, were collected.

CRediT authorship contribution statement

Riccardo Chiarcos: Writing – original draft, Formal analysis, Conceptualization. **Katia Sparnacci:** Methodology, Investigation. **Diego Antonioli:** Investigation, Formal analysis, Data curation. **Chiara Ivaldi:** Investigation, Data curation. **Valentina Gianotti:** Supervision, Methodology. **Riccardo Po:** Writing – original draft, Formal analysis, Conceptualization. **Paolo Biagini:** Supervision, Conceptualization. **Simona Losio:** Methodology, Investigation. **Michele Laus:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2024.113148.

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