

# Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide in the Presence of Functional Transfer Agents Provides Telechelic Polycarbonates: Synthesis of CO<sub>2</sub>-Containing Macromonomers and Macroinitiators

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One possible way to store the excess CO<sub>2</sub> present in atmosphere is to use it as a reagent for the synthesis of commodities. In particular, CO<sub>2</sub> and epoxides can be copolymerized to produce a large variety of polycarbonates which appear very promising in various application fields. Further, the addition of an appropriate transfer agent in the reaction mixture promotes the formation of telechelic polycarbonates which can be used where specific functional polymers are necessary. In this work, (hydroxyethyl) methacrylate and 2-hydroxyethyl-2-bromoisobutyrate species are exploited as transfer agents in the copolymerization of CO<sub>2</sub> and cyclohexene oxide, in the presence of a macrocyclic phenolate dimagnesium catalyst. The effect of the transfer agent concentration on the polycarbonate characteristics is evaluated. Finally, the obtained telechelic polycarbonates are used as macromonomers and macroinitiators in the synthesis of statistical and block copolymers.

high chemical inertness of CO<sub>2</sub>, a large number of catalytic systems has been explored since the Inoue's seminal work published in 1969.<sup>[5]</sup> Nowadays, among the most promising systems are salen metal catalysts<sup>[6]</sup> and macrocyclic phenolate dimetallic catalysts,<sup>[7]</sup> introduced, respectively by the Darensbourg and Williams groups. A typical salen metal catalyst, represented in **Figure 1a**, contains a central metal cation which is coordinated by both salen and X ligands, where X can be a Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or AcO<sup>-</sup> ion.<sup>[6]</sup> Typical metals used for the central cation are chrome,<sup>[8]</sup> cobalt,<sup>[9]</sup> and aluminum.<sup>[10]</sup> Further, salen metal catalysts generally require the addition of cocatalyst species such as the neutral nucleophile

4-dimethylaminopyridine (DMAP) or bis(triphenylphosphine) iminium salts PPNX, in which X can be Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, AcO<sup>-</sup>, or 2,4 dinitrophenolate anions.<sup>[11–16]</sup> When this kind of catalyst is employed, the copolymerization reaction is carried out generally at a temperature ranging from 50 °C to 100 °C and pressure comprised between 10 and 50 bar.<sup>[17]</sup> Milder conditions are required

## 1. Introduction

Aliphatic polycarbonates are currently widely studied as they can be directly synthesized through the copolymerization of carbon dioxide (CO<sub>2</sub>) and epoxides; thus, providing a viable route for the storage and reuse of CO<sub>2</sub> in commodities.<sup>[1,2,3,4]</sup> Due to the

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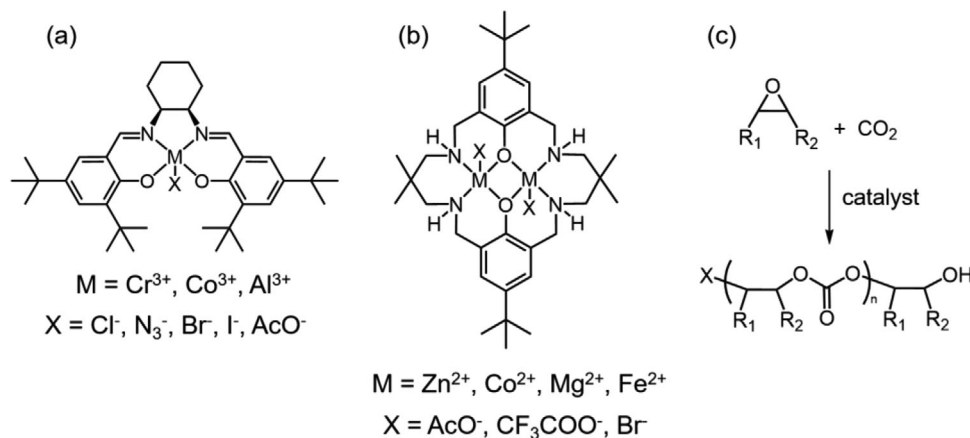
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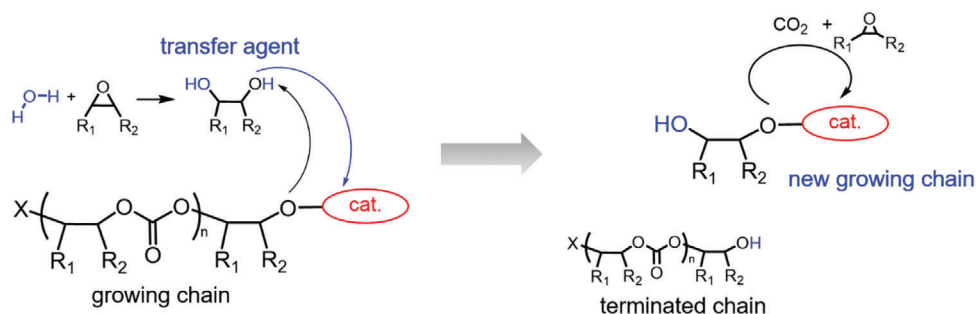
**Figure 1.** Generic structure of a) salen metal catalysts and b) macrocyclic phenolate dimetallic catalysts. c) Copolymerization of  $\text{CO}_2$  and epoxides to provide an aliphatic polycarbonate.  $R_1$  and  $R_2$  indicate generic substituent groups of the epoxide.

for macrocyclic phenolate dimetallic catalysts, which guarantee the same yield and selectivity of salen catalysts but at temperatures lower than  $80^\circ\text{C}$  and pressures close to the atmospheric one.<sup>[7]</sup> The reduction of pressure is undoubtedly advantageous both from the economics of the process and as guarantee of safety. A representative picture of these catalysts is provided in Figure 1b. In these cases, the phenolate macrocycle coordinates two central metal cations, which can be identical to or different from each other.<sup>[18,19]</sup> Typical metals are zinc,<sup>[20]</sup> cobalt,<sup>[21]</sup> magnesium,<sup>[22]</sup> and iron.<sup>[23]</sup> Again, additional X-ligands are coordinated to the metal centers and typical X are  $\text{AcO}^-$ ,  $\text{CF}_3\text{COO}^-$  (trifluoroacetate group), and  $\text{Br}^-$ .<sup>[22]</sup> The presence of additional cocatalysts is not required. Interestingly, it was recently demonstrated that these catalysts can also be used in the depolymerization of the polycarbonates to  $\text{CO}_2$  and epoxides, opening up the prospect for a recycling process of the material in a perspective of total environmental sustainability.<sup>[24–26]</sup> Regardless to the employed catalyst, the copolymerization generally starts from the X ligand, which also has the role of initiator and proceeds by alternating the entry of  $\text{CO}_2$  and epoxides in the growing chain.<sup>[27]</sup> This results in a polycarbonate having an X species and a hydroxy moiety (OH) as the two end-groups, as represented in Figure 1c.

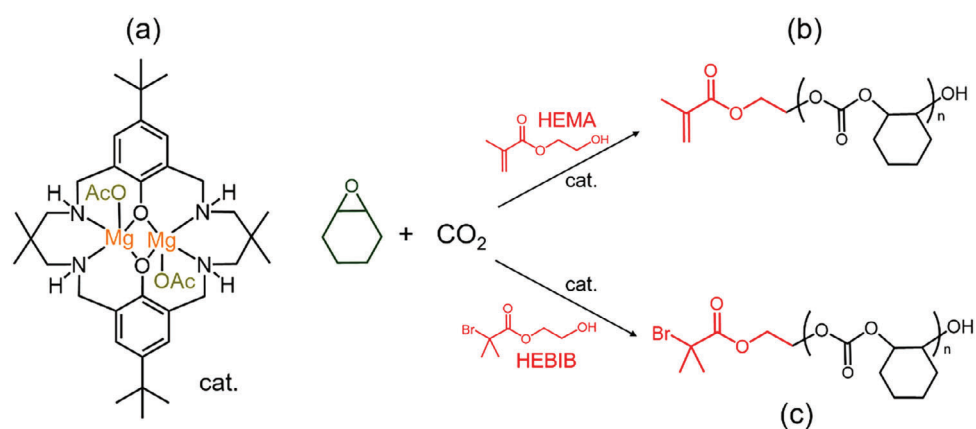
The most investigated epoxides for the copolymerization with  $\text{CO}_2$  are undoubtedly the propylene oxide (PO) and the cyclohexene oxide (CHO), which result in the polypropylene carbonate (PPC) and the polycyclohexene carbonate (PCHC), respectively.<sup>[28,29]</sup> PPC is a high-toughness polymer but lacks mechanical properties suitable for structural applications whereas PCHC is characterized by thermal and mechanical properties similar to the ones of polystyrene.<sup>[30]</sup> Unfortunately, PCHC is an extremely brittle material and none of the attempts to modify its structure by varying the structure of the epoxy monomer have improved this characteristic.<sup>[31]</sup> Further, the relatively low degradation temperature of these polymers, that is generally below  $300^\circ\text{C}$ , makes the material processing difficult.<sup>[31]</sup> For this reason, aliphatic polycarbonates can hardly be competitive products both as elastomer and in the rigid plastic world.<sup>[2,31]</sup>

A completely different scenario occurs if such polycarbonates are evaluated as novel functional materials. In this perspective, the use of polycarbonates containing functional end/side-

groups brings interesting perspectives in different fields such as biomedicine,<sup>[32–39]</sup> composites,<sup>[2,31]</sup> energy storage,<sup>[40]</sup> and microelectronics,<sup>[41,42]</sup> with the only limit being the creativity of the polymer scientist. Incidentally, it is interesting to observe that telechelic PPCs having the two end-groups constituted by hydroxy groups are already marketed as special polyols for the synthesis of polyurethanes.<sup>[43,44,45]</sup> If the insertion of specific side groups can be achieved by selecting appropriate epoxides and, possibly, using post-polymerization reactions, the most practical way to synthesize telechelic polycarbonates probably consists in exploiting the chain transfer processes that can occur in parallel to the main reaction. In fact, free alcohol species are typically generated during the polymer synthesis from the reaction of water traces with epoxide monomers. The resulting diols lead to protonation of the growing polycarbonate chains, resulting in termination and the formation of new growing chains,<sup>[2,4,8]</sup> as represented in Figure 2. This chain transfer mechanism is ubiquitous in the aliphatic polycarbonate synthesis, regardless of the employed catalyst.<sup>[22,27,46,47,48]</sup> Of course, the obtained polymers have a hydroxy initial group if the transfer process is promoted by water molecules,<sup>[46]</sup> but different functionalities can be inserted using specific transfer agents.<sup>[46,49]</sup> For example, when PO is copolymerized with  $\text{CO}_2$  by using a cobalt salen catalyst in the presence of both phosphonic and phosphoric acids as transfer agents, linear and branched phosphorated PPC displaying flame-retarding properties are obtained.<sup>[50]</sup> Beyond this, alcohols and carboxylic acids are undoubtedly among the most used transfer agents.<sup>[51–54]</sup> For example, polycarbonates containing ionic groups were obtained using, as transfer agents,<sup>[55]</sup> ionic liquids comprising hydroxy or carboxy functionalities. In a similar manner, polycarbonates containing metal complexes in the main chain were synthesized using special transfer agents consisting of diols comprising the metal complex between the two hydroxyl moieties.<sup>[56]</sup> A carboxy/trithio-carbonate transfer agent was instead used to synthesize PPCs and PCHCs comprising, at one end, a group able to perform a RAFT (radical addition-fragmentation chain-transfer) reaction.<sup>[57]</sup> In this way, these telechelic polycarbonates were used as macroinitiators to polymerize vinyl monomers; thus, leading to block copolymers. Alternatively,  $\alpha$ -halocarboxylic acids were used as transfer agents to produce PPC and PCHC



**Figure 2.** Chain transfer mechanism operated by water molecules during the copolymerization of a generic epoxide and  $\text{CO}_2$ .



**Figure 3.** a) Chemical structure of the used macrocyclic phenolate dimagnesium catalyst. Copolymerization of CHO and  $\text{CO}_2$  in the presence of catalyst and either b) HEMA or c) HEBIB as the transfer agent.

macroinitiators comprising, at one end, groups able to perform an ATRP (atom transfer radical polymerization) synthesis. Also in this case, block copolymers<sup>[58]</sup> were obtained.

Interestingly, when macrocyclic phenolate dimetallic catalysts<sup>[49]</sup> were employed, only simple alcohols and amines with no functional moieties were evaluated as transfer agents. This is quite surprising due to the remarkable versatility and stability of such catalytic systems. Therefore, in the present work, both (hydroxyethyl) methacrylate (HEMA) and 2-hydroxyethyl-2-bromoisobutyrate (HEBIB) are evaluated as model transfer agents for the copolymerization of CHO and  $\text{CO}_2$  in the presence of a macrocyclic phenolate dimagnesium catalyst with the final goal to obtain under mild conditions, respectively, PCHC-based macromonomers and macroinitiators suitable for the preparation of bottlebrush and block copolymers. Although some scientific papers already report the use of transfer agents containing a halide group for the synthesis of macroinitiators,<sup>[58]</sup> the present paper reports, for the first time, the use of an alcohol-containing methacrylate (HEMA) as a model transfer agent for the synthesis of polycarbonate-based macromonomers.

## 2. Results and Discussion

CHO and  $\text{CO}_2$  were copolymerized in the presence of the macrocyclic phenolate dimagnesium catalyst represented in **Figure 3a**. CHO was dried on calcium hydride before use; while, the catalyst was synthesized in a glove box and preserved under inert

atmosphere. The initial molar ratio between CHO and catalyst was fixed at the value of 1000 in all reactions. Both HEMA and HEBIB species were used as transfer agents, with initial molar ratios ( $R$ ) between the transfer agent and catalyst of 10, 30, 50 and 70. The polymers obtained with HEMA were signed as  $m\text{PCHC}_n$ , where  $m$  indicates the presence of a methacrylic end-group and  $n$  indicates the  $R$  value used in the synthesis. When HEBIB was employed, the obtained polymers were signed as  $\text{BrPCHC}_n$ , with Br indicating the presence of a bromine end-group and  $n$  having the same meaning as before. A further comparative polymer was synthesized without the addition of transfer agents and was referred to as  $\text{PCHC}_0$ . All reactions were carried out for 24 h at  $80^\circ\text{C}$  and  $\text{CO}_2$  pressure of 4 bar. Specifically, the lowest temperature among those explored in the literature was selected to carry out the reaction under mild conditions. Similarly, the pressure was chosen close to atmospheric pressure.<sup>[22]</sup> In this context, it is worth mentioning that with these catalysts, the  $\text{CO}_2$  pressure did not significantly affect the molecular weight of the obtained polymer.<sup>[22]</sup> The details of the synthesis condition of each sample are reported in **Table 1** whereas a schematic representation of the copolymerization reactions in the presence of either HEMA or HEBIB is reported in **Figure 3b,c**.

The CHO conversion after 24 h reaction time was evaluated by  $^1\text{H-NMR}$  spectroscopy, as indicated in **Figure S1**, Supporting Information for the sample  $m\text{PCHC}_{10}$ . All spectra are included in the Supporting Information correlated with the relative

**Table 1.** The type of transfer agent and the initial molar ratio between the transfer agent and the catalyst ( $R$ ) used in the synthesis are reported for each sample. The expected molecular weight of the polymer, indicated as  $M_{n,EXP}$  and calculated considering that all chains start from the transfer agent and supposing that the polymerization is living in nature, is included in the table. The experimental number average molecular weight ( $M_n$ ), the dispersity index ( $\mathcal{D}$ ), the fraction of functional polymers ( $F$ ), and the glass transition temperature ( $T_g$ ) of the samples are also reported. In all synthesis, the initial molar ratio between CHO and catalyst was 1000, the temperature was set at 80 °C, the CO<sub>2</sub> pressure was 4 bar, and the reaction time was 24 h.

Sample	Transfer agent	$R$	$M_{n,EXP}$ <sup>a)</sup> [g mol <sup>-1</sup> ]	$M_n$ <sup>b)</sup> [g mol <sup>-1</sup> ]	$\mathcal{D}$ <sup>b)</sup>	$F$ <sup>c)</sup>	$T_g$ <sup>d)</sup> [°C]
mPCHC <sub>10</sub>	HEMA	10	10 900	3700	1.15	0.64	82
mPCHC <sub>30</sub>	HEMA	30	3300	1700	1.20	0.73	70
mPCHC <sub>50</sub>	HEMA	50	1900	1250	1.20	0.89	54
mPCHC <sub>70</sub>	HEMA	70	1300	850	1.25	0.86	40
BrPCHC <sub>10</sub>	HEBIB	10	6500	3300	1.25	0.51	80
BrPCHC <sub>30</sub>	HEBIB	30	2300	1800	1.20	0.75	69
BrPCHC <sub>50</sub>	HEBIB	50	1600	1150	1.20	0.86	57
BrPCHC <sub>70</sub>	HEBIB	70	1100	900	1.25	0.80	44
PCHC <sub>0</sub> <sup>a)</sup>	—	—	71 000	9400	1.27	—	108

<sup>a)</sup> This was calculated considering that all chains start from the transfer agent; and therefore, using the equation  $M_{n,EXP} = (1000/R) \times 142 \times C_{CHO}$ , where 1000 is the initial molar ratio between CHO and catalyst, 142 is the molecular weight of the repeating unit, and  $C_{CHO}$  is the monomer conversion (reported for each sample in the Supporting Information). In the sample PCHC<sub>0</sub>  $R$  was set equal to 1; <sup>b)</sup>  $M_n$  and  $\mathcal{D}$  values were obtained from SEC analysis; <sup>c)</sup>  $F$  values were calculated from <sup>1</sup>H-NMR spectra, as discussed later in the text; <sup>d)</sup>  $T_g$  values were obtained from differential scanning calorimetry (DSC) analysis carried out between -25 °C and 140 °C with heating/cooling ramps of 10 °C min<sup>-1</sup>.

conversion values. CHO conversions ranging from 50% to 70% were observed.

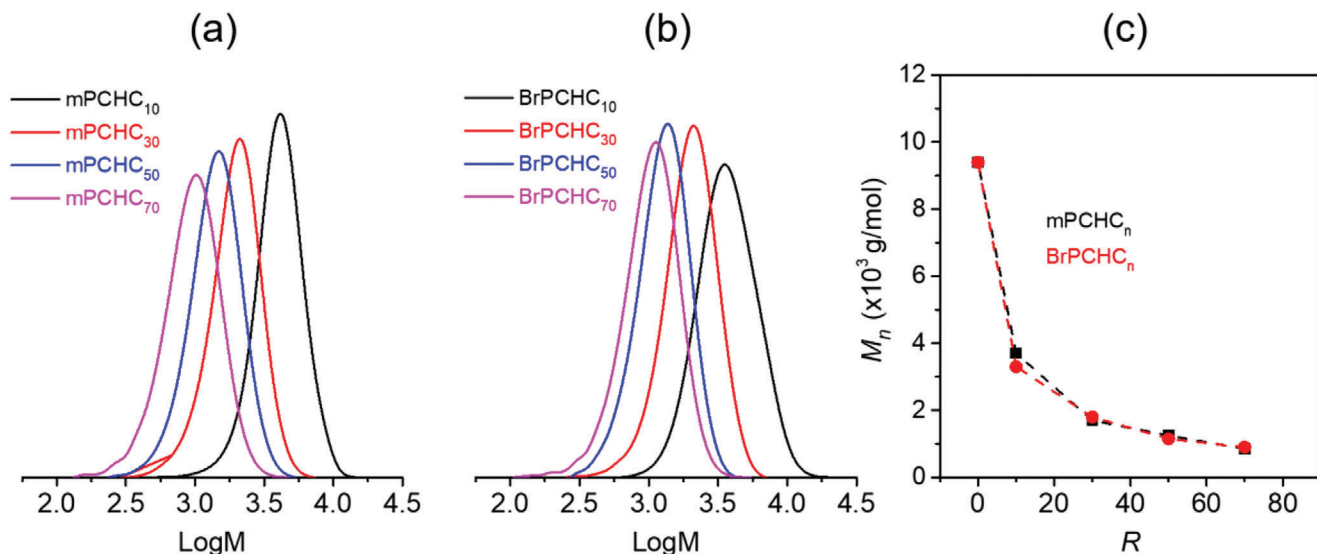
The copolymerization reaction was turned off lowering the CO<sub>2</sub> pressure, putting the reaction mixture in contact with atmosphere, and diluting the raw material with dichloromethane. The polymers were purified by dissolution in dichloromethane followed by precipitation in cold n-hexane.

The molecular weight ( $M_n$ ) and the dispersity index ( $\mathcal{D}$ ) of the polymers were determined by size exclusion chromatography (SEC). The chromatograms obtained for the mPCHC<sub>*n*</sub> and BrPCHC<sub>*n*</sub> samples are reported in Figures 4a,b, respectively, while  $M_n$  and  $\mathcal{D}$  values are collected in Table 1. Furthermore,  $M_n$  is reported as a function of  $R$  in Figure 4c. Corresponding to the same  $R$  value, the molecular weights of both mPCHC<sub>*n*</sub> and BrPCHC<sub>*n*</sub> were very similar and strongly decreased from 3500 up to 900 g mol<sup>-1</sup> with increasing  $R$ . In all cases,  $M_n$  was remarkably lower than the value of 9400 g mol<sup>-1</sup> obtained for the PCHC<sub>0</sub> sample in which no transfer agent was added. Interestingly, the very similar  $M_n$  values for the same  $R$  indicated that the effect of the transfer agents was very similar. Relatively low values of  $\mathcal{D}$  (< 1.25) were observed. It is important to observe that for all samples, the experimental  $M_n$  was remarkably lower than the expected one (indicated as  $M_{n,EXP}$ ), calculated considering that all chains start from the transfer agent and that the polymerization has a living nature. The  $M_{n,EXP}$  of each sample is reported in Table 1. The difference between  $M_n$  and  $M_{n,EXP}$  can be explained considering a significant role of water traces in pro-

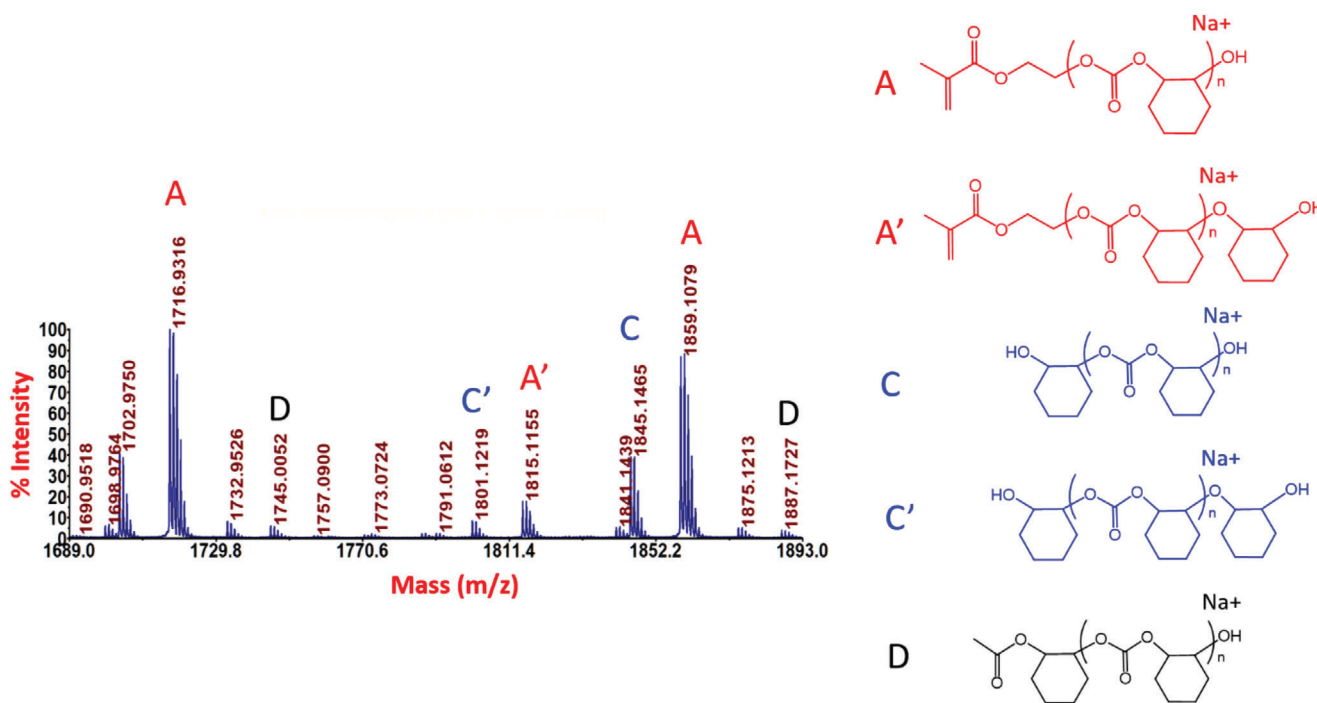
moting chain transfer reactions in competition with the transfer agent.<sup>[2,4,8]</sup> The role of water was particularly evident in the sample PCHC<sub>0</sub>, in which no transfer agent was employed but in which  $M_n$  was approximately one seventh of the expected value. Interestingly, the relevance of chain transfer reactions promoted by water decreased as the amount of the added transfer agent increased, as indicated by the convergence of  $M_n$  and  $M_{n,EXP}$  at the highest  $R$  values.

In order to have direct information on the nature of the polymer end-groups, MALDI-TOF analysis was carried out on both mPCHC<sub>*n*</sub> and BrPCHC<sub>*n*</sub> samples. Full spectra of all samples are included in the Supporting Information. As an example, portions of spectra of mPCHC<sub>70</sub> and BrPCHC<sub>70</sub> in the region between 1689 and 1893 are reported in Figures 5 and 6, respectively together with the chemical structures of the different species. In both polymer samples, the prevailing structure is the one containing the transfer agent moiety as one of the two end-groups and a hydroxy group as the other one. Such species are labeled as A for mPCHC<sub>70</sub> and B for BrPCHC<sub>70</sub>, whereas A' and B' indicate the same species containing an ether bond randomly placed along the chain. These defects are generated by the consecutive insertion of two epoxides in the main chain and are widely observed in this type of polymerization.<sup>[6]</sup> The spectrum of BrPCHC<sub>70</sub> also reveals a species B," which corresponds to the species B in which the bromine end-group is removed. The loss of a halogen atom probably occurs during the MALDI-TOF experiment as already reported in literature.<sup>[14,59]</sup> Remarkably, both spectra reveal the presence of polymers containing a hydroxy-group on both the chain ends. Such species are identified as C and C'. This observation confirms that water continues to play a relevant role in the chain transfer process, also in the presence of transfer agents. However, it is important to underline that species C and C' are present in a much smaller quantity compared to A (B) and A' (B') that actually contain the functional group brought about by the transfer agent. Finally, traces of polycarbonates having an acetate end group, deriving from the catalyst, are observed in both spectra and such species are identified as D. This species is the first to be generated during the synthesis before the transfer process occurs. Situations qualitatively similar are found for all the other polymers, as reported in Figures S8–S15, Supporting Information. A schematic representation of the processes that lead to the formation of the molecular species described above is also reported in Figure S16, Supporting Information.

Aside the minor amount of the acetate-terminated species, there are essentially two types of species in mPCHC<sub>*n*</sub> and BrPCHC<sub>*n*</sub> samples: PCHCs with the end-groups consisting of one in the HEMA or HEBIB moiety and the other in a hydroxy-group (species A and A' in the first case and B, B', and B'' in the second one) and dihydroxy-terminated PCHCs (species C and C'). Since for the subsequent use of such polymers as either macromonomers or macroinitiators a high degree of functionalization is preferable, a quantitative measurement of the actual fraction of the functional polymers is necessary. This fraction is indicated as  $F$  and represents the ratio between the number of chains terminated with a HEMA or HEBIB group and the total number of chains contained in the sample. The measurement of  $F$  was carried out by <sup>1</sup>H-NMR spectroscopy. Full spectra of all samples are included in the Supporting Information, whereas the spectra with signal assignment for mPCHC<sub>70</sub> and BrPCHC<sub>70</sub>



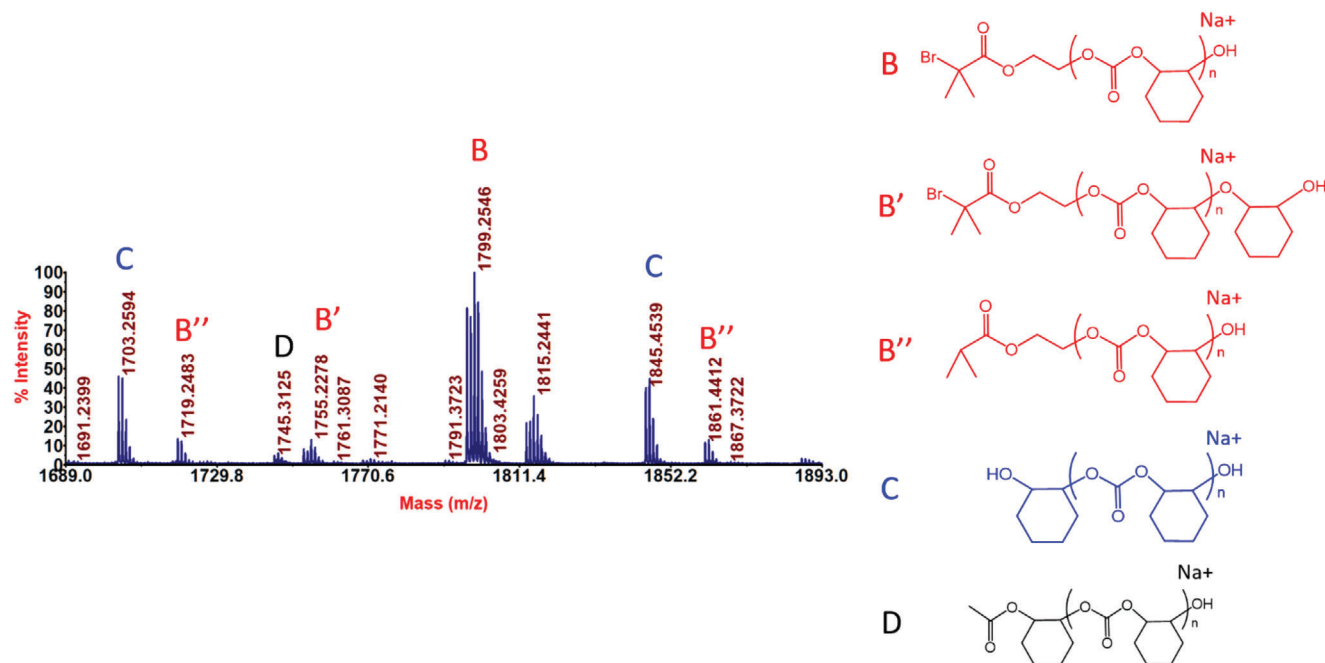
**Figure 4.** SEC curves of the a) mPCHC<sub>n</sub> and b) BrPCHC<sub>n</sub> samples. c) The  $M_n$ s of the samples as a function of initial molar ratio between the transfer agent and the catalyst ( $R$ ) is also reported.



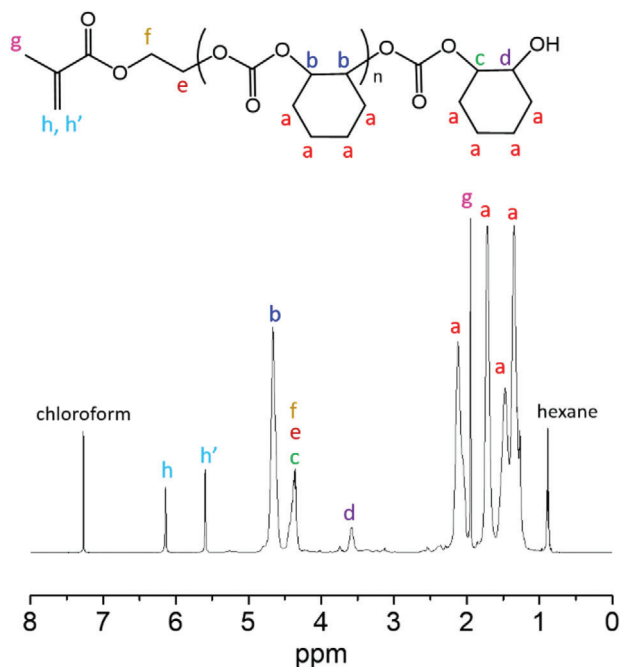
**Figure 5.** MALDI-TOF spectrum of the mPCHC<sub>70</sub> sample (zoom). The structures of the most abundant species are also reported.

samples are reported in **Figures 7** and **8**, respectively, as a typical example. The signal assignment of the end-group protons c and d was already reported in literature,<sup>[26]</sup> whereas the assignment of the protons e and f, related to the transfer agent moiety, came from simple spectra simulations. For mPCHC<sub>n</sub>,  $F$  could be estimated from the intensity of h, h' signals, relative to the methacrylic double bond, and the intensity of d signal. The detailed formula is contained in Equation (S1), the Supporting Information. In the case of mPCHC<sub>70</sub>, a  $F$  value of 0.87 was ob-

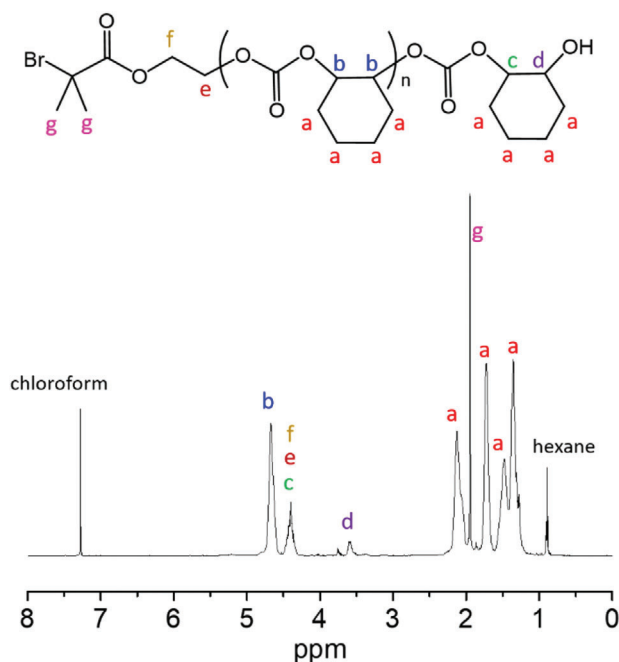
tained. Alternatively,  $F$  could be also calculated using the signals relative to the protons c, d, e and f, without considering h and h'. Also in this case, the detailed formula is reported in Equation (S2), Supporting Information. The value of  $F$  for mPCHC<sub>70</sub> obtained from this alternative set of signals was 0.86. Similar accordance between the two approaches was obtained for all the mPCHC<sub>n</sub> samples, thus supporting the assignment of protons e and f. The real advantage of the second approach is that it can be applied to BrPCHC<sub>n</sub> samples, in which no clear signals of



**Figure 6.** MALDI-TOF spectrum of the BrPCHC<sub>70</sub> sample (zoom). The structures of the most abundant species are also reported. Incidentally, the species with *m/z* of 1815 are equivalent to the species B but with K<sup>+</sup> as the ionizing cation instead of Na<sup>+</sup>.



**Figure 7.** <sup>1</sup>H-NMR spectrum of the sample mPCHC<sub>70</sub>. Signal assignments are also reported.



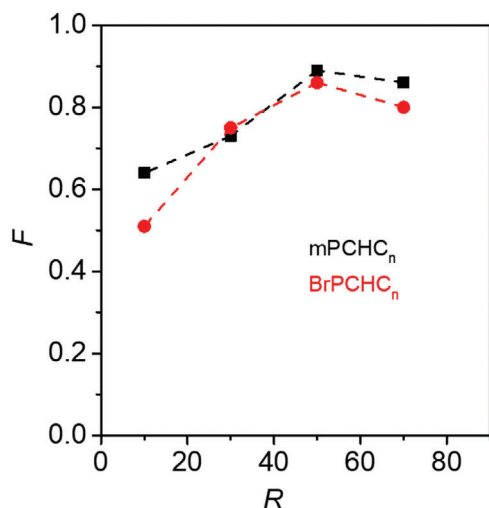
**Figure 8.** <sup>1</sup>H-NMR spectrum of the sample BrPCHC<sub>70</sub>. Signal assignments are also reported.

the functional end-group are present. The *F* value obtained for BrPCHC<sub>70</sub>, reported in Figure 8 was 0.80.

**Figure 9** reports *F* as a function of *R* for both mPCHC<sub>*n*</sub> and the BrPCHC<sub>*n*</sub>. The percentage of functional chains increases as the amount of transfer agent increases until *F* is close to ≈80%

and then levels off. No significant differences were observed between the mPCHC<sub>*n*</sub> and the BrPCHC<sub>*n*</sub> samples, thus confirming a comparable activity of the two transfer agents.

Finally, the glass transition temperature (*T*<sub>g</sub>) of each sample was determined by differential scanning calorimetry (DSC). The



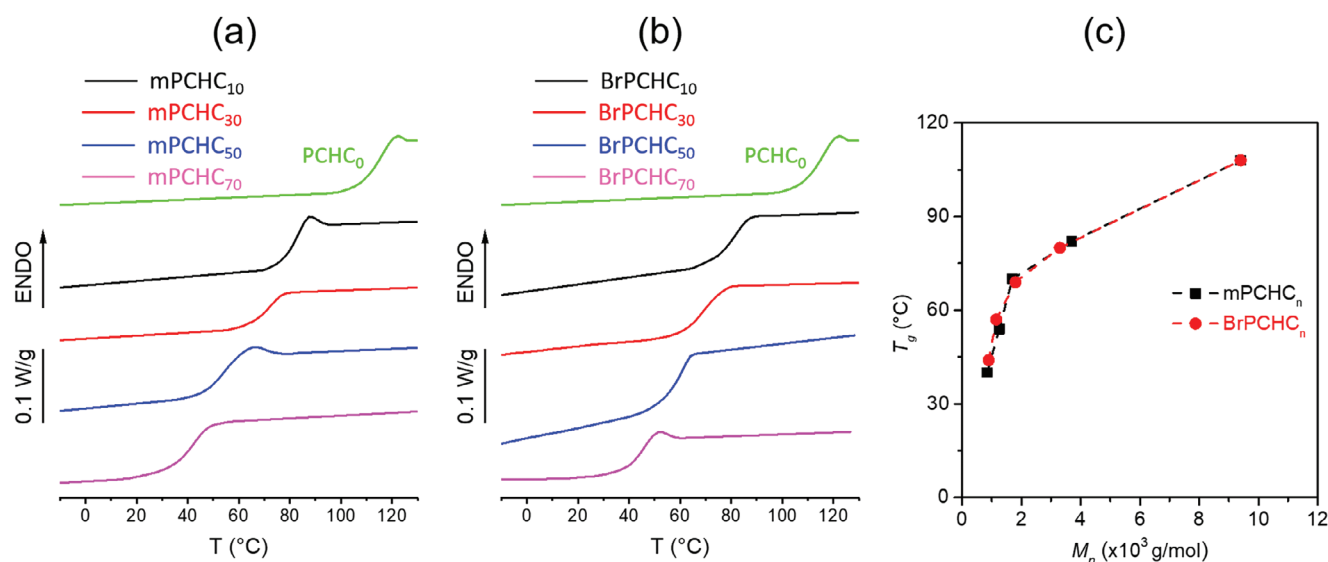
**Figure 9.** Molar fraction of functional polymer ( $F$ ) as a function of the initial molar ratio between the transfer agent and the catalyst ( $R$ ) for the mPCHC $_n$  and the BrPCHC $_n$  samples.

obtained thermograms are reported in **Figure 10a,b** for samples mPCHC $_n$  and BrPCHC $_n$ , respectively. Further, the evaluated  $T_g$  values are included in **Table 1** and reported in **Figure 10c** as a function of  $M_n$  of the polymer.  $T_g$  increased regularly as  $M_n$  increased, with values of  $\approx 42$  °C for the polymers with the lower molecular weight up to 108 °C for PCHC $_0$ , in good accordance with literature.<sup>[31]</sup> The nature of the end-group did not seem to significantly influence the  $T_g$ .

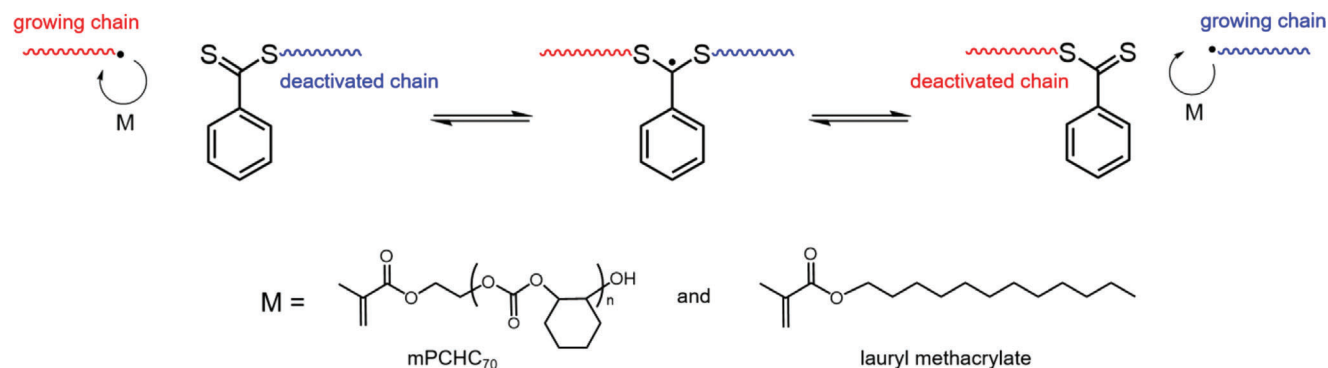
### 2.1. Synthesis of Statistical and Block Copolymers Containing PCHC

As typical example, mPCHC $_{70}$  sample was employed as a methacrylic macromonomer for the synthesis of statisti-

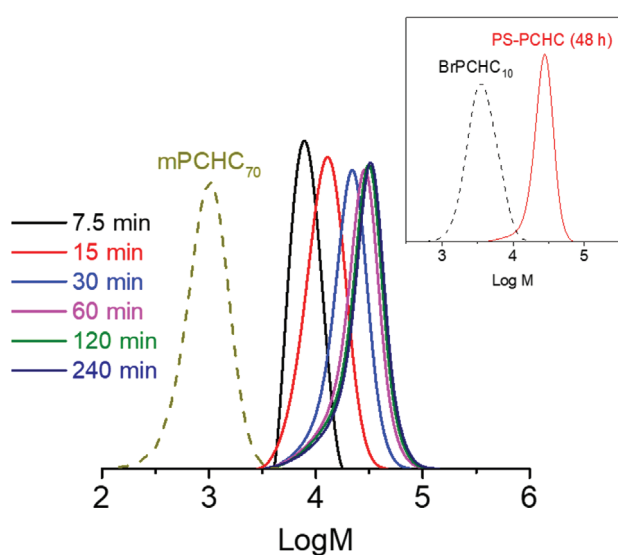
cal copolymers containing side PCHC chains. In particular, mPCHC $_{70}$  was mixed with lauryl methacrylate, keeping their molar ratio equal to 12, and the mixture underwent a RAFT polymerization<sup>[57,60,61]</sup> using azobisisobutyronitrile (AIBN) as initiator and 2-cyano-2-propyl benzodithioate (DTB) as the RAFT agent. In RAFT polymerizations, polymers with controlled molecular weights and low dispersity indexes are obtained by the continuous activation/deactivation process of the growing chains mediated by the RAFT agent.<sup>[57,60,61]</sup> A schematic representation of this process for the current system is provided in **Figure 11**. The initial molar ratio between monomers and DTB was 150; while, the ratio between DTB and AIBN was 2. The reaction was carried out at 90 °C in Schlenk flasks for different times ranging from 7 to 240 min. The reaction mixtures were finally analyzed by  $^1\text{H-NMR}$  spectroscopy to determine the monomer conversion and, consequently, the copolymer composition. Full spectra are included in the Supporting Information whereas monomer conversion and polymer composition are reported in **Table S1** Supporting Information. The lauryl methacrylate appeared more reactive than mPCHC $_{70}$ ; thus, leading to an enrichment of lauryl methacrylate units in all the copolymers, especially corresponding to short reaction times. The copolymers were finally purified by precipitation in cold methanol, and the molecular weights were determined by SEC analysis. It is important to note that all the mPCHC $_n$  polymers, except mPCHC $_{10}$ , are soluble in methanol. Therefore, both the unreacted functionalized chains and the non-functionalized chains contained in the mPCHC $_{70}$  sample were removed during the precipitation process. The obtained SEC curves are reported in **Figure 12**, whereas the molecular weight and the dispersity index of the samples are included in **Table S1** Supporting Information. The molecular weight of the copolymer increases with reaction time from 7700 to 24 900 g mol $^{-1}$ ; while, the dispersity index also increases from 1.08, for the shortest time, to 1.26 for the longest synthesis. The increase of the molecular weight with conversion and the relatively low dispersity indexes confirm the possibility to use



**Figure 10.** DSC thermograms of the a) mPCHC $_n$  and b) BrPCHC $_n$  samples. c) The  $T_g$  of each sample as a function of the molecular weight ( $M_n$ ) is also reported.



**Figure 11.** Schematic representation of the RAFT reaction carried out on the monomer mixture containing mPCHC<sub>70</sub> and lauryl methacrylate in the presence of DTB as the RAFT agent.



**Figure 12.** SEC curves of the statistical copolymers obtained from the copolymerization of the mPCHC<sub>70</sub> sample and lauryl methacrylate. The SEC curve of the purified block copolymer obtained using the BrPCHC<sub>10</sub> sample as a macroinitiator is reported in the inset.

functionalized PCHC as macromonomers in controlled radical polymerizations.

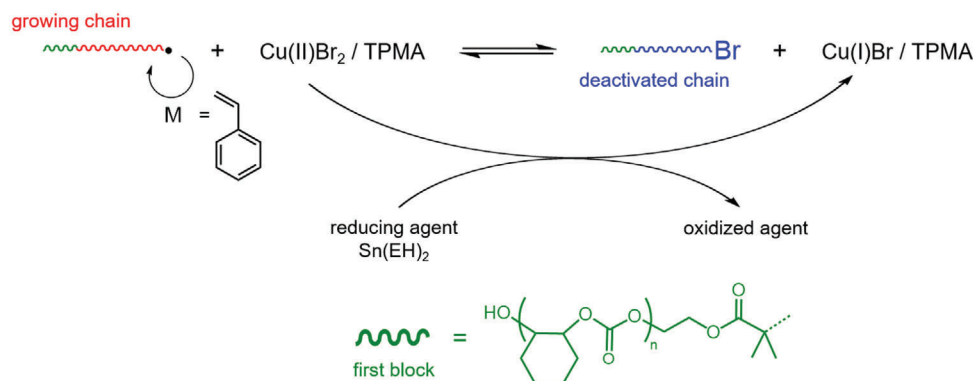
The BrPCHC<sub>10</sub> sample was instead tested as macroinitiator for the synthesis of a poly(styrene-*b*-PCHC<sub>10</sub>) block copolymer via the ARGET-ATRP (Activators ReGenerated by Electron Transfer-ATRP) approach.<sup>[58,62,63]</sup> In this reaction, the activation/deactivation process discussed before for RAFT polymerizations is promoted by a metal catalyst consisting of a copper halide salt, as schematically shown in **Figure 13**. For the sake of clarity, in ARGET type of ATRP reactions, as in the present case, a reducing agent is also employed to reduce the metal contained in the catalyst. In particular, copper (II) bromide (CuBr<sub>2</sub>) was used as the catalyst, tin (II) 2-ethylhexanoate [Sn(EH)<sub>2</sub>] as the reducing agent, and tris[(2-pyridyl)methyl]amine (TPMA) as the ligand. The initial molar ratio between styrene and BrPCHC<sub>10</sub> was 150; while, the ratios [BrPCHC<sub>10</sub>]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[Sn(EH)<sub>2</sub>]<sub>0</sub>/[TPMA]<sub>0</sub> were 1/0.02/0.2/0.22. The reaction was carried out at 90 °C for 48 h in a Schlenk flask. The polymer was then purified

by precipitation in cold methanol and analyzed by SEC (the curve is reported in Figure S32, Supporting Information). A polystyrene block was clearly grown starting from the BrPCHC<sub>10</sub> macroinitiator, increasing the overall molecular weight of the polymer. However, a residue of unreacted chains appeared at low molecular weights, consistent with the fact that not all the PCHC chains were HEBIB functionalized, as discussed before (see Figure 9). The sample was then fractionated by SEC in order to separate the block copolymer species from the unreacted PCHC. The SEC curve of the purified block copolymer is reported in the inset of Figure 12, indicating an increase in the molecular weight from 3300 to 24 200 g mol<sup>-1</sup> with a dispersity index of 1.14. Due to the close glass transitions of the polymers making the two blocks, a single step due to the glass transition process of the copolymer was observed at 95 °C in the DSC thermogram (Figure S34, Supporting Information). Finally, the NMR spectrum, which is included in the Supporting Information, revealed that the copolymer had a molar percentage of PCHC of 10% and a mass percentage of PCHC of 13%. This copolymer composition might be compatible with the self-assembly of the sample in to regular packed sphere patterns.<sup>[64]</sup> In this sense, different patterns can be designed by changing the dimension and the composition of the block copolymer in order to produce lithographic masks with exceptionally reduced dimensions, thus making polycarbonate-based copolymers as an extremely promising tool in microelectronic processes.<sup>[41,42]</sup> The synthesis approach discussed in this work presents a feasible way to obtain such copolymers, facilitating their use in the most varied fields such as device production and precision doping of silicon.<sup>[62,65,66,67]</sup>

### 3. Conclusion

Polycyclohexene carbonates having methacrylate and halide end-groups are synthesized by copolymerizing cyclohexene oxide and CO<sub>2</sub> in the presence of a macrocyclic phenolate dimagnesium catalyst and an appropriate transfer agent. Both the molecular weight and the degree of functionalization of the polymers depend significantly on the amount of transfer agent used during the synthesis. In particular, as the amount of transfer agent increases, the molecular weight of the polymer decreases; while, the degree of functionalization increases. A methacrylate-terminated sample is successfully employed as macromonomer





**Figure 13.** Schematic representation of the ARGET-ATRP reaction carried out on styrene using BrPCHC<sub>10</sub> as the macroinitiator.

for the synthesis of statistical copolymers having relatively long side chains consisting of cyclohexene carbonate units. On the other hand, a halide-terminated sample is used as macroinitiator for the synthesis of a poly(cyclohexene carbonate-*b*-styrene) block copolymer with potential applications in nanolithography. The possibility of effectively obtaining functional polycarbonates under the mild conditions required by the macrocyclic dimagnesium phenolate catalyst opens the door to the easy development of new macromolecular systems.

#### 4. Experimental Section

**Materials:** Cyclohexene oxide was purchased by Merck and dried on calcium hydride before use. The macrocyclic phenolate dimagnesium catalyst was synthesized as described in literature.<sup>[22]</sup> Lauryl methacrylate and styrene were purchased by Merck and purified with an inhibitor removal column before use. All other reagents were purchased by Merck and used as received.

**Synthesis of the Functional PCHCs:** The synthesis of the mPCHC<sub>10</sub> was reported as a typical example. 5 mL of CHO (0.05 mol), 36 mg of catalyst (0.05 mmol), and 61 μL of HEMA (0.5 mmol) were added in a pressure reactor (Buchi Miniclave) in a MBRAUN LABstar glove box. CO<sub>2</sub> gas was added to the reactor and the reaction was carried out at the constant pressure of 4 bar, at 80 °C and for 24 h. After this time, the reactor was opened and 5 mL of dichloromethane was added to the reaction mixture. 0.2 mL of a solution consisting of hydrochloric acid in methanol (5% in weight) was also added.<sup>[26]</sup> The polymer was then purified by precipitation in cold *n*-hexane and dried under vacuum.

The other mPCHC<sub>*n*</sub> and BrPCHC<sub>*n*</sub> samples were obtained in the same way by appropriately changing the type and the amount of the transfer agent.

**Synthesis of Statistical Copolymers Using mPCHC<sub>70</sub> as a Macromonomer:** 2.0 g (2.35 mmol) of mPCHC<sub>70</sub>, 7.2 g (28.24 mmol) of lauryl methacrylate, 45.0 mg (0.20 mmol) of DTB, 16.7 mg (0.10 mmol) of AIBN, and 9 mL of anisole were mixed together and stirred. The mixture was divided in six Schlenk flasks and degassed by three freeze–thaw cycles. The reactions were carried out at 90 °C for 7.5, 15, 30, 60, 120, and 240 min in nitrogen atmosphere. The polymers were then purified by precipitation in cold methanol and dried under vacuum.

**Synthesis of the Block Copolymer Using BrPCHC<sub>10</sub> as a Macroinitiator:** 10 mL (87 mmol) of styrene, 1.91 g (0.58 mmol) of BrPCHC<sub>10</sub>, 3.37 g (0.01 mmol) of TPMA, 2.60 g (0.01 mmol) of CuBr<sub>2</sub>, and 5 mL of anisole were mixed together and stirred in a Schlenk flask. The mixture was degassed by two freeze–thaw cycles. A mixture consisting of 47.0 mg (0.12 mmol) of Sn(EH)<sub>2</sub>, 33.7 mg (0.12 mmol) of TPMA, and 1 mL of anisole was added to the Schlenk flask, and one more freeze–thaw cycle was performed. The reaction was carried out at 90 °C for 48 h under

nitrogen atmosphere. The polymer was purified by precipitation in cold methanol and dried under vacuum.

**Polymer Characterization:** SEC analysis was performed with a 590 Waters chromatograph equipped with Waters HSPgel HR3 and HR4 columns and a refractive index detector. The analysis was carried out at 25 °C using THF as the solvent at the flow rate of 0.3 mL min<sup>-1</sup>. The calibration curve was obtained using polystyrene standards with molecular weight ranging from 500 to 30 000 g mol<sup>-1</sup>.

<sup>1</sup>H-NMR analysis was performed at room temperature in deuterated chloroform with a 500 MHz Bruker instrument.

A 4800 MALDI TOF/TOF analyzer (Applied Biosystems, Framingham, MA, USA) was used to acquire the MALDI-TOF spectra. The instrument was equipped with a Nd:YAG laser with 355 nm wavelength of <500 ps pulse and 200 Hz repetition rate. MALDI-TOF mass spectra were recorded in reflectron and positive ion mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]malononitrile DCTB (20 mg mL<sup>-1</sup> in THF) was used as a matrix, whereas sodium trifluoroacetate (NaTFA) 0.1 M in THF was added as cationization agent. Polymer, matrix, and cationization agent solution volumes were mixed to obtain 5:25:2 ratios. 1 mL of each sample/matrix/cationization agent mixture was spotted on the MALDI-TOF sample holder and slowly dried to allow crystallization. The resolution of the MALDI-TOF spectra ranged from 5000 to 8000 FWHM, whereas the accuracy of mass determination ranged from 80 to 120 ppm.

DSC analysis was carried out by a Mettler–Toledo Calorimetry mod. 821e instrument on ≈5 mg of polymer placed in alumina crucibles. Heating and cooling ramps of 10 °C min<sup>-1</sup> were performed between –25 °C and 140 °C.

#### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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#### Conflict of Interest

The authors declare no conflict of interest.

#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

cyclohexene/CO<sub>2</sub> copolymerization, dimagnesium catalyst, macroinitiator, macromonomer, telechelic polycyclohexene carbonate, transfer agent

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