

# Controlled Synthesis of Statistical Polycarbonates Based on Epoxides and CO<sub>2</sub>

Alina Denk, Emilia Fulajtar, Carsten Troll, and Bernhard Rieger\*

The controlled synthesis of terpolymer structures is often limited by the intrinsic reactivities of the monomers. For the synthesis of a statistical terpolymer from cyclohexene oxide (CHO) and propylene oxide (PO) with CO<sub>2</sub>, an instrumental solution is demanded. Implementing a setup where one monomer can be added to the reaction mixture over the whole course of the reaction, the random distribution of the epoxides over the whole chain is realized. The successful terpolymerization can be determined with diffusion-ordered nuclear magnetic resonance spectroscopy and gel permeation chromatography measurements while the statistical microstructure of the generated polymers is indicated in NMR spectroscopy and differential scanning calorimetry measurements. Furthermore, the concept is transferred to the terpolymerization of limonene oxide with PO and CO<sub>2</sub> underlining the versatility of the setup.

## 1. Introduction

The development of CO<sub>2</sub>-based aliphatic polycarbonates (PCs) in 1969 by the group of Inoue<sup>[1]</sup> set the starting point for research ambitions on this class of polymer materials which has not decreased since then. Until today, the range of monomers that can be used in the reaction is extended constantly. While bisphenol A-based polycarbonates (BPA-PCs) depend on fossil sources, the group of aliphatic PCs provide the opportunity to utilize sustainable feedstocks for epoxide monomers and furthermore the incorporation of CO<sub>2</sub> as a C1 building block.<sup>[2,3]</sup> The catalyst used in this work is based on the catalysts of Coates et al., a  $\beta$ -diimine (BDI) zinc complex.<sup>[4]</sup> In the improved complex from Rieger et al. CF<sub>3</sub> groups increase the Lewis acidity of the zinc center and N(TMS)<sub>2</sub> is used as initiating group.<sup>[5]</sup> With this catalyst a broad

variety of epoxides can be copolymerized with CO<sub>2</sub> to the corresponding PCs. Through the combination of two different epoxides in the reaction solution even terpolymers can be synthesized (Scheme 1).<sup>[5]</sup>

In this work, we strive for the synthesis of terpolymers based on two different epoxides and CO<sub>2</sub>. Thus, we want to control the microstructure of the polymers and combine the mechanical and thermal properties of the individual copolymers via terpolymerization.

## 2. Results and Discussion

### 2.1. Differences in Reaction Speed

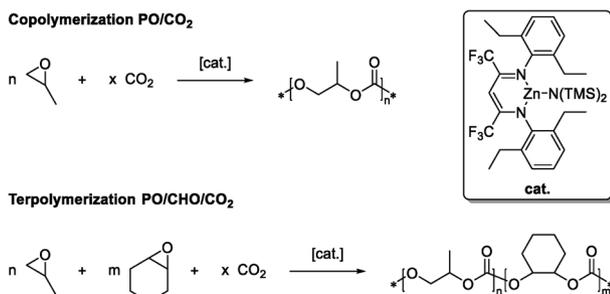
While the catalyst allows to copolymerize a broad variety of epoxides with CO<sub>2</sub>, they show strong differences in their reaction speed. This is clearly visible in the direct comparison of the copolymerizations of cyclohexene oxide (CHO), limonene oxide (LO), and propylene oxide (PO) each with CO<sub>2</sub>, which can be followed using in situ IR. The signal of the respective PCs formed is plotted against time in Figure S1 (Supporting Information). While CHO is completely converted after only 40 min, the copolymerization of PO takes more than 20 h. The polymerization speed of these monomers depends on the catalyst and can vary for different catalytic systems. In the case of standard one pot terpolymerizations two epoxides would be placed in the reactor together with the catalyst and pressurized with CO<sub>2</sub>. Due to the strong difference in reaction speed the more reactive epoxide would then be incorporated into the growing polymer chain more frequently than the other, less reactive, epoxide. Over the course of the reaction the concentration of the faster incorporated monomer in the reaction mixture would therefore decrease more rapidly and with this the probability to incorporate this monomer would also decrease over time. The resulting terpolymer microstructure is therefore of a gradient type (see Figure S3, Supporting Information). In our work we target a controlled incorporation of both monomers resulting in a statistical copolymer structure. In such a statistical copolymer no segment of measurably different composition is observed.<sup>[6]</sup> Such a uniform monomer distribution can result in consistent properties over the whole polymer chain. In this case no microphase separation or amphiphilic behavior is observed as it is possible for block or gradient copolymers. Statistical polymers from monomers with such different reactivities as for our reaction system can only be realized by controlling the polymerization process and incorporation of each monomer by means

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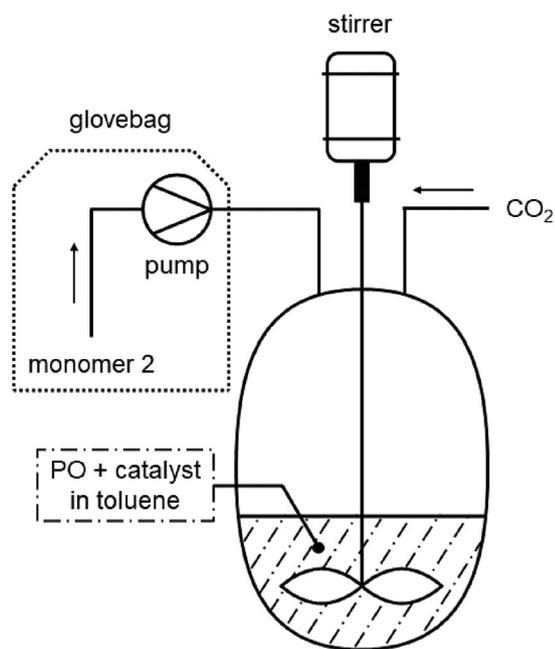
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**Scheme 1.** Copolymerization of propylene oxide (PO) with CO<sub>2</sub> and terpolymerization of PO, cyclohexene oxide (CHO), and CO<sub>2</sub> with a  $\beta$ -diimine zinc complex as catalyst (cat.).



**Figure 1.** Setup of the dosing system for the synthesis of statistical terpolymerization of two epoxides and CO<sub>2</sub>.

of instrumental modifications. Regulating the concentration of both monomers in the reaction mixture during the whole terpolymerization time, the generated microstructure of the evolving polymer chain can be controlled. A reduced concentration of the faster incorporated epoxide allows the other monomer to insert into the growing chain more frequently. This can be achieved by dosing the faster epoxide into the reaction mixture, keeping its concentration low for less dominance in the terpolymerization process.

## 2.2. Setup Dosing System

The instrumental layout for this controlled terpolymerization resembles a semi-batch setup (Figure 1). A pump is used to constantly dose the second monomer against a CO<sub>2</sub> pressure of 30 bar into the autoclave. The mass flow is monitored with a mass flow meter which is installed between the pump and the autoclave. With the in situ IR of the autoclave system the progress of

the polymerization can be tracked. To ensure a water-free storage and transfer of the second monomer into the autoclave the storage flask and pump are placed in a glove bag under nitrogen and connected via steel capillaries with the autoclave. The atmosphere in the glove bag is furthermore dried with phosphorus pentoxide (P<sub>4</sub>O<sub>10</sub>) as desiccant.

## 2.3. Statistical Terpolymerization of PO, CHO, and CO<sub>2</sub>

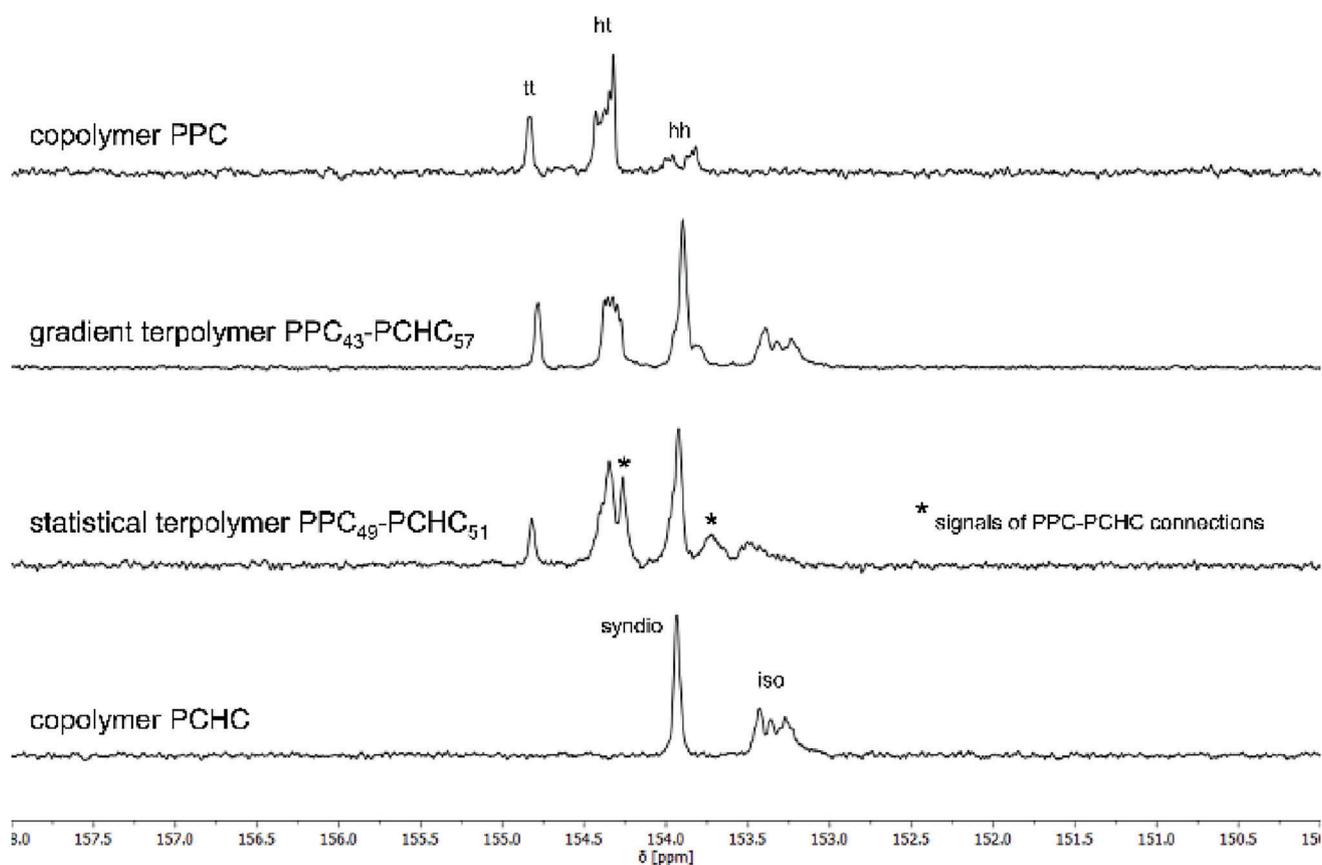
In the terpolymerization procedure PO and catalyst solution are introduced into the reactor and pressurized with CO<sub>2</sub>. The second monomer is then added via the dosing system at a constant feed rate. Table 1 shows terpolymerizations with different feeds of PO and CHO. Since CHO is dosed into the reaction mixture with a constant rate until stopping the reaction, the conversion is never 100%. At the same time the conversion of PO should stay below 100% as well to have both monomers present in the reaction mixture during the whole polymerization time. The difference between the classic batch approach and the herein presented semi-batch process can be observed via in situ IR (Figure S2, Supporting Information). The constant dosing of the second monomer ensures a constant reaction of both monomers and therefore also a linear growth of the intensity of the polymer signal. CHO reacts with CO<sub>2</sub> selectively towards the polymer product, PO forms besides poly(propylene carbonate) (PPC) also cyclic propylene carbonate (cPC) as a thermodynamically stable side product.<sup>[7]</sup> The selectivity of cPC formation could be decreased to around 20% by reducing the reaction temperature to 25 °C.<sup>[8]</sup> With an increasing CHO feed (Table 1, entries 4 and 5) the backbiting during the ongoing polymerization forming cPC (Scheme S1, Supporting Information),<sup>[9]</sup> is suppressed since CHO is inserted rapidly into the end of the growing chain. The composition and molecular weight of the generated terpolymers can be controlled by the feed rate and time and by adjusting the ratio between PO, CHO, and catalyst. A high amount of PO in the reactor together with the dosing rate of CHO reduced to a minimum result in a terpolymer with a PPC content of 76% (Table 1, entry 1). With the same dosing rate, but a longer reaction time (Table 1, entries 2 and 3) or with a higher rate and short reaction time (Table 1, entries 4 and 5) the amount of poly(cyclohexene carbonate) (PCHC) in the terpolymer can be further increased. The resulting polymers are analyzed via <sup>1</sup>H NMR to determine the ratio between PPC and PCHC in the product (Figures S4–S8, Supporting Information). They also show narrow mass distributions ( $\mathcal{D} \leq 2.0$ ) as expected for the selective generation of terpolymers (Figures S11–S15, Supporting Information). To analyze the polymers further we used diffusion-ordered NMR spectroscopy (DOSY-NMR) measurements, where the signals of both PPC and PCHC share a diffusion coefficient (Figure S9, Supporting Information). This indicates a connection of both polymers in one molecule and therefore successful terpolymerization.

Besides the polymerization of PO, CHO, and CO<sub>2</sub> towards connected terpolymers we were interested in the microstructure of the polymers, since we aimed for a statistical distribution of the epoxides over the whole polymer chain. To analyze this, we measured <sup>13</sup>C NMR of the polymers and compared specifically the carbon signals of the carbonyl moiety of the synthesized terpoly-

**Table 1.** Polymerizations of PO/CHO/CO<sub>2</sub> toward statistical PPC-PCHC terpolymers.

Entry	Feed <sup>a)</sup> PO:CHO:cat.	Dosing rate CHO [mL h <sup>-1</sup> ]	Time [h]	Conversion <sup>b)</sup> PO, CHO [%]	Selectivity <sup>c)</sup> PPC:cPC [%]	PPC:PCHC [% <sup>c)</sup>	M <sub>n</sub> (Đ) [kg mol <sup>-1</sup> ] <sup>d)</sup>
1	2000:190:1	0.12	7	28, 72	77:23	76:24	91.0 (1.2)
2	1000:470:1	0.12	18	81, 90	81:19	61:39	60.9 (1.8)
3	500:380:1	0.12	16	81, 89	82:18	49:51	37.2 (2.0)
4	500:430:1	0.48	5	24, 85	100:0	25:75	33.8 (1.7)
5	250:910:1	0.96	4	53, 91	100:0	14:86	99.2 (1.4)

Polymerizations in toluene, 30 bar CO<sub>2</sub> pressure, 25 °C, stirred at 500 rpm. <sup>a)</sup>Feed of CHO calculated from the sum of CHO and PCHC signals in <sup>1</sup>H NMR with the sum of PO, cPC, and PPC signals as reference. <sup>b)</sup>Calculated from the respective polymer and monomer integrals in <sup>1</sup>H NMRs. <sup>c)</sup>Calculated from the respective (polymer) signals in <sup>1</sup>H NMRs. <sup>d)</sup>Measured via GPC in THF relative to poly(styrene) standards.



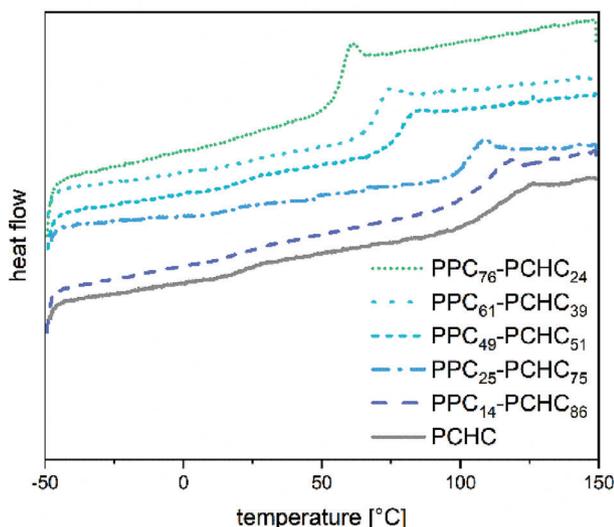
**Figure 2.** Carbonyl signals in the <sup>13</sup>C NMR of the pure copolymers PPC and PCHC. Compared to gradient and statistical PPC-PCHC terpolymers.

mers with pure PPC and PCHC and a gradient terpolymer synthesized via the classic one pot procedure (**Figure 2**).

In the NMR of PPC it can be distinguished between tail-to-tail (tt), head-to-tail (ht), and head-to-head (hh) connection of the PO units.<sup>[10]</sup> These three signals can be found as well in the NMRs of the terpolymers since both terpolymers don't have a strictly alternating epoxide incorporation. The tacticity of PCHC originates from the orientation of its cycle resulting in syndiotactic (syndio) or isotactic (iso) moieties.<sup>[11]</sup> In the case of both terpolymer NMRs the hh signal overlaps with the signal of syndiotactic PCHC, but only the statistical terpolymer shows the evolution of new signals (\*) in the <sup>13</sup>C NMR, presumably caused by an increased number of carbonyls connecting PO and CHO with each other.

#### 2.4. Statistical Terpolymerization of PO, LO, and CO<sub>2</sub>

To show the versatility of the approach using a dosing system to control the microstructure we investigated LO in the statistical terpolymerization with PO and CO<sub>2</sub>. In Table S1 (Supporting Information) these terpolymerizations are summarized. The reaction speed of LO is lower than of CHO, as indicated in Figure S1 (Supporting Information), which is why the dosing rates were reduced to avoid accumulation of LO in the reaction mixture. For the calculations of feed and conversion it must be noted, that the synthesized LO contains 92% of the *trans*-isomer. That is important since *cis*-LO is not accessible for the polymerization towards poly(limonene carbonate) (PLC) with our catalyst system and re-



**Figure 3.** DSC measurements of PCHC and PPC-PCHC terpolymers with ratios in subscript.

mains unreacted in the reaction solution. Via this procedure terpolymers with a tailored ratio of PPC and PLC in the final product could be synthesized. These polymers show narrow mass distributions (1.5–1.6) in gel permeation chromatography (GPC) measurements (Figures S16–S19, Supporting Information), but also carbonyl signals in  $^{13}\text{C}$  NMR at 152–153 ppm, that origin from PPC-PLC connections in the terpolymer (Figure S10, Supporting Information). These signals indicate a successful synthesis of statistical terpolymers as explained for PPC-PCHC before.

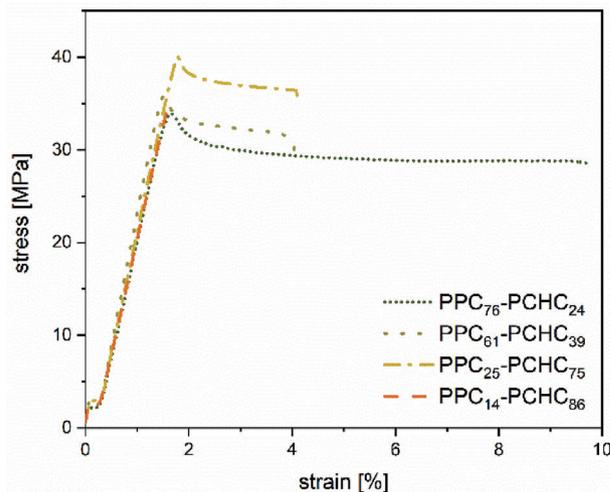
### 2.5. Thermal Properties

To analyze the thermal properties of the generated polymers differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were performed and the results are summarized in Table S2 (Supporting Information). As expected the terpolymers show mixed glass transition temperatures ( $T_g$ ) since both epoxides are incorporated statistically and therefore influence each other's thermal behavior. With an increasing amount of PPC in the terpolymer the  $T_g$  decreases (Figure 3 and Figure S20, Supporting Information).

The thermal stability of the terpolymers is analyzed via TGA. Here the onset decomposition temperature ( $T_d$ ) shows with increasing PPC content only a minor decrease from 293 to 262 °C for PPC-PCHC and to 244 °C for PPC-PLC (Figures S21 and S22, Supporting Information). Compared to pure PPC with a  $T_d$  of 180 to 240 °C<sup>[12]</sup> the terpolymers of PPC with PCHC show an increase in thermal stability.

### 2.6. Mechanical Characterization

The terpolymers were furthermore examined in tensile testing of dog bone shaped specimen. For the PPC-PCHC terpolymers an increase in elongation at break with increasing PPC content could be observed while the E-modulus remained high at over



**Figure 4.** Tensile testing of specimen from PPC-PCHC terpolymers.

2500 MPa (Figure 4). For the composition of 76:24 (PPC:PCHC) an elongation at break of 10% could be measured. In the case of PPC-PLC terpolymers this trend was not as clear. The E-moduli of 2070 to 2470 MPa for these samples were similarly high, as well as the tensile strengths of around 40 MPa. However, the elongation at break showed only minor increases up to 3% for a PPC content of 65%.

## 3. Conclusion

With the application of a dosing system, we were able to add one epoxide monomer in the terpolymerization of two epoxides and  $\text{CO}_2$  into the reactor during the whole polymerization process. This way we could control the ratio of the monomers in the reaction mixture and therefore their incorporation into the terpolymer chain. Despite the major differences in reactivity of the epoxides this control over the monomer feed allowed us to synthesize statistical terpolymers with tailored ratios of the polymers in the terpolymer chain. Low polydispersities and high molecular weights show the stability of the polymerization process despite the continuous feed into the ongoing reaction. An increasing PPC content in the terpolymer led to a decreasing mixed  $T_g$  of the terpolymer, but the thermal stability remained high. An influence on the mechanical properties is given, but not as prominent as observed for the thermal behavior. With an increasing PPC content the elongation at break in tensile testing increased for the PPC-PCHC terpolymers.

## 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

aliphatic polycarbonates, carbon dioxide, copolymer engineering, dosing systems, statistical terpolymers

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[1] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287.

- [2] Y. Xu, L. Lin, M. Xiao, S. Wang, A. T. Smith, L. Sun, Y. Meng, *Prog. Polym. Sci.* **2018**, *80*, 163.
- [3] S. J. Poland, D. J. Darensbourg, *Green Chem.* **2017**, *19*, 4990.
- [4] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738.
- [5] M. Reiter, S. Vagin, A. Kronast, C. Jandl, B. Rieger, *Chem. Sci.* **2017**, *8*, 1876.
- [6] J. Zhang, B. Farias-Mancilla, M. Destarac, U. S. Schubert, D. J. Keddie, C. Guerrero-Sanchez, S. Harrisson, *Macromol. Rapid Commun.* **2018**, *39*, 1800357.
- [7] G. W. Coates, D. R. Moore, *Angew. Chem., Int. Ed.* **2004**, *43*, 6618.
- [8] S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284.
- [9] G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, *Chemistry* **2005**, *11*, 6298.
- [10] D. J. Darensbourg, in *Synthetic Biodegradable Polymers* (Eds: B. Rieger, A. Künkel, G. W. Coates, R. Reichardt, E. Dinjus, T. A. Zevaco), Springer, Berlin, Heidelberg, **2012**, pp. 1–27.
- [11] C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky, G. W. Coates, *Dalton Trans.* **2006**, 237.
- [12] O. Phillips, J. M. Schwartz, P. A. Kohl, *Polym. Degrad. Stab.* **2016**, *125*, 129.