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Investigation and Comparison of Catalytic Methods to Produce Green CO_2-Containing Monomers for Polycarbonates

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Abstract: The preparation of CO_2-containing polymers with improved degradation properties is still very challenging. An elegant method for preparing these polymers is to use CO_2-containing monomers in ring-opening polymerizations (ROP) which are particularly gentle and energy-saving methods. However, cyclic carbonates are required for this which are not readily available. This paper therefore aims to present the optimization and comparison of two synthesis methods to obtain cyclic carbonates for ROP. Within this work, cyclic styrene carbonate was synthesized from readily available raw materials by using a Jacobsen catalyst for the reaction of styrene oxide and carbon dioxide or an organocatalyst for the transesterification of methyl carbonate with 1-phenyl-1,2-ethanediol. The latter performed with 100% selectivity to the desired styrene carbonate, which was succesfully tested in ROP, producing an amorphous thermoplastic polymer with a T_G of 185 °C.

Keywords: CO_2-containing monomers; ring-opening polymerization; cyclic styrene carbonate; polystyrene carbonate; green chemistry; bifunctional catalyst system; organocatalytic; Jacobsen catalyst; polycarbonate; CO_2 utilization

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1. Introduction

Three hundred ninety-one million tons of polymer were produced worldwide in 2022, essentially from petroleum-based feedstocks [1]. Incorporation of carbon dioxide (CO_2) into polymers is one of the most promising areas of current research for entering into a carbon cycle in chemical mass production.

Ethylene oxide (EO) has been used to produce polymers for over 70 years. A partial or complete substitution would be desirable as the production of this monomer causes high costs and environmental pollution. This idea was first made possible and published with the copolymerization of ethylene oxide and CO_2 with zinc catalysts [2]. Although replacing ethylene oxide with carbon dioxide makes ecological sense, this approach has not made its way to the market so far [2–4]. Further catalysts and variations in the product structures are still being researched today [2,3,5–14]. The synthesis of CO_2-containing polymers is still very challenging, aiming at the avoidance of high-energy costs during copolymerization and extreme conditions such as high temperatures and pressures. Using pre-formed CO_2-containing monomers such as cyclic ethylene carbonate (cEC) opens up new possibilities in this area with ring-opening polymerizations (ROPs), whose reaction pathways are already better understood [7,8,10,15]. By using ROP, the incorporation of CO_2 is substantially increased in comparison to CO_2/epoxide copolymerization, and therefore ensures significant savings in energy and raw materials.

From this point of view, the possibility of using CO_2 as a starting material for polymer production leads to great added value for the environment, also because of the simplified recycling option. Crude oil-based products are usually recycled via energy-intensive pyrolysis or cracking into small molecules and basic chemicals. By incorporating CO_2, predetermined breaking points are created that facilitate processing and enable easy recovery of the monomers. There are various very efficient ways of producing CO_2-based monomers [2,3,13,16,17]. One of the most important monomers is cEC, which is produced in large quantities via the so-called Omega process as an intermediate in ethylene glycol production [7,8,15,18–20] (see Figure 1).

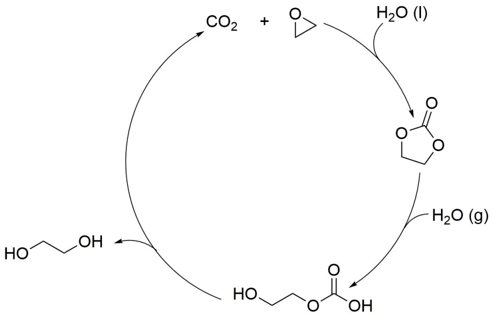

Figure 1. Large-scale synthesis of cyclic ethylene carbonate (cEC) via the Omega process.

This monomer is suitable not only for producing CO_2-containing polymers employing controllable ring-opening polymerization but also for producing CO_2-containing surfactants, if a long-chain alcohol is used as starter for the ROP [8,9].

However, access to other CO_2-containing cyclic carbonate monomers is more challenging. In this work, we would like to focus primarily on a CO_2-containing alternative for the synthesis of polystyrene. Using the example of cEC, discussed above as an alternative for the production of CO_2-containing alternatives for polyethylene oxide, cyclic styrene carbonate (cSC) would be an alternative CO_2-containing monomer building block for polystyrene carbonate. The production of cyclic styrene carbonate (cSC) as monomers for these polymers is accessible using different synthesis methods [21–23].

This results in a network for the production of modern alternative CO_2-containing polymers such as poly(ethylene ether carbonate) from cEC or polystyrene carbonate from cyclic styrene carbonate (see Figure 2) [11,21,22,24,25].

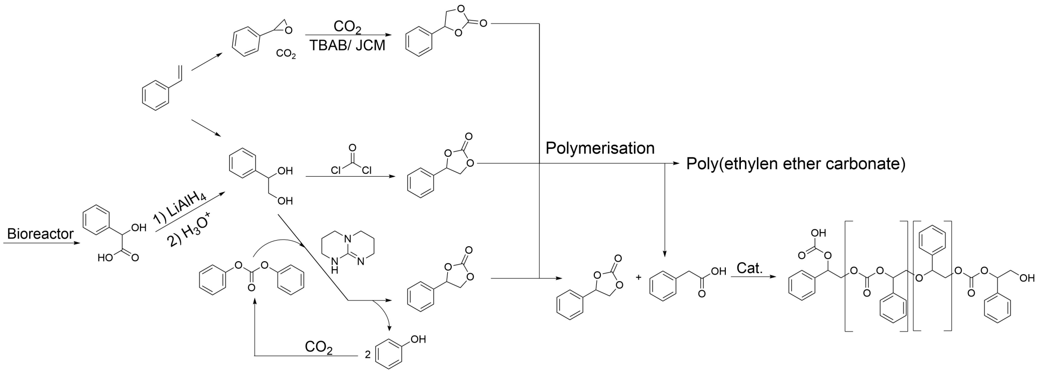

Figure 2. Possible production routes from CO_2 to the CO_2-containing polymer.

Due to strict environmental and safety requirements regarding the hazardous nature of phosgene, the phosgenation route is not considered in this study. However, this route might be suitable in industry with the appropriate equipment [26,27]. Therefore, only catalytic synthesis methods are considered, which already provide good yields of 90% or more [21,22]. For the desired synthesis of monomer for a ring-opening polymerization, these routes need to be modified, as the complete separation of phenol and benzonitrile is very demanding and not suitable for industrial processes, as it is only possible via column chromatography. Therefore, the objective of this work is a solution to this problem by adapting the synthesis. One alternative is a catalytic reaction of CO_2 and styrene epoxide at elevated pressure. However, this synthesis has already proven to be problematic in the literature, as problems with side reactions such as polymerization have been observed here [28]. Therefore, yields of only between 60 and 90% were reported [11,22,24,29–32].

It is desirable to produce these polymers and, at the same time, control the product properties by using a CO_2 building block such as cEC or cSC. The understanding of the control possibilities [8] in ring-opening polymerization (ROP) results in a tunability of the reaction, which leads to the adjustment of both the melting point and the CO_2 content [6,13,33,34]. However, the melting point is also determined to some extent by the structure of the polymers [33].

However, to achieve these control options, pure CO_2-containing monomers are essential. Although a variety of synthesis methods provide access to the cyclic carbonates, only a few are commercially available, such as cEC. For producing polystyrene carbonate, cyclic styrene carbonate is required as a monomer of the ROP. This can be produced in several ways as shown in Figure 2. These are primarily divided into high-pressure reactions with gaseous CO_2 catalyzed by homogeneous catalysts and the organocatalysis converting linear carbonates with dioles by transesterification. Still, both methods have disadvantages that make them unattractive for larger scale applications. High-pressure autoclave reactions of epoxides and CO_2 sometimes yield very impure products, some of which are already polymerized and have to be separated [6,13,35–37], as some of the catalyst degradation products themselves act as catalysts for the ROP [8,13,33,38,39]. This leads to purification processes with high equipment and energy costs. In addition, the high pressure (10–30 bar CO_2) and the high requirements for safe operation of a high-pressure reactor make this process itself unattractive. The influence of the individual parameters on the reaction must also be clarified. A review of the reaction of epoxides with CO_2 at bifunctional catalysts revealed that the reaction is highly sensitive to pressure and temperature in addition to the exact dosage of two catalyst components [40]. The most promising results have been obtained so far with the so-called Jacobson catalyst that was chosen also for this study (see Figure 3).

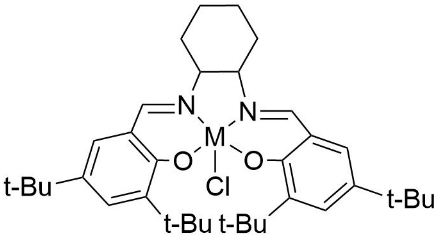

Figure 3. Structure of the Jacobsen catalyst (**M** = Mn or Co).

As an alternative, as well as a more controllable method [6,11,13,29,40,41], organocatalysis has already attracted some interest, as the chemicals used avoid high-pressure processes and can theoretically be run in closed-loop processes [21,22,36] and are based on renewable raw materials (reduced mandelic acid). The reaction also leads to high conversion of the raw material avoiding intensive separations [21,22]. The problem with this reaction, however, is the recycling of the coupled product as the reaction is mostly carried out with diphenyl carbonate (DPC). However, this leads to the complex problem of phenol separation, as this is itself a high-boiling product and is structurally like the target product which is not feasible on an industrial scale. Finding an alternative with a more effective solvent as well as another carbonate reagent such as dimethyl carbonate (DMC) [22] are central parts of this paper.

This study focuses on the following research questions:

- What effect does pressure have on the product distribution of the autoclave reaction?
- What effect does the temperature have on the autoclave reaction?
- What influence do the concentrations of the two catalysts have?
- Can an optimized synthesis of cyclic styrene carbonate by organocatalysis be an alternative to the homogeneously catalyzed reaction?

2. Results and Discussion

2.1. CO_2 High-Pressure Synthesis of Styrene Carbonate

To determine the effect of selected parameters, experiments were conducted varying the temperature, pressure, and concentration of the catalysts. It was found that the homogeneous high-pressure reaction is highly dependent on these parameters. We could validate literature towards the successful formation of cyclic carbonate for the standard parameters [24]. However, through ATR-IR measurement, and visible differences regarding the viscosity of the reaction samples, the presence of cyclic carbonate (cSC), linear carbonate (lSC), and a polymer species (pSC) are identified in all samples (see Figure 4). All products from the autoclave experiments show in subsequent investigations using HPLC-ESI-DAD that even under optimized conditions, polymerization takes place to a certain degree.

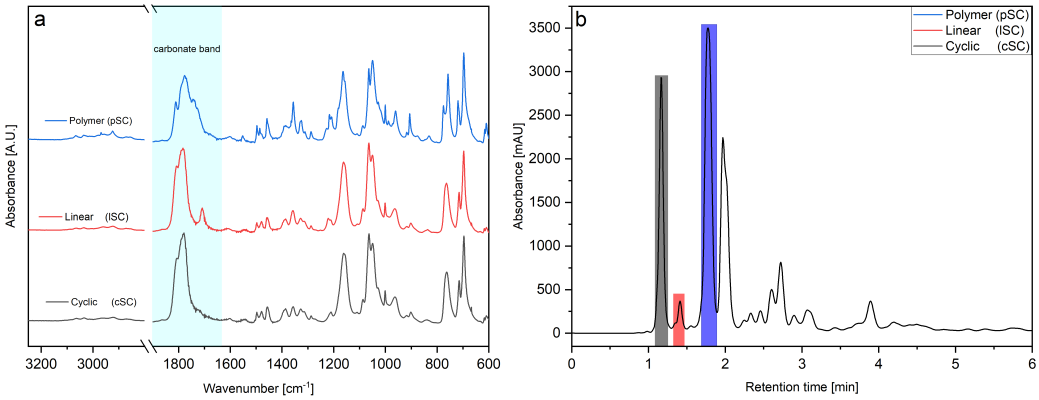

Figure 4. Identification of the polymeric (blue), linear (red), and cyclic (black) carbonate band through (**a**) ATR-IR spectra and (**b**) HPLC-ESI-DAD measurements.

Due to the required predominant formation of either lSC and cSC, we investigated the reaction pathway through collecting samples over the course of the reaction. We observe cSC as the first species formed in all samples (see Figure 5), and whereas styrene oxide is consumed and the reaction proceeds, gradually the concentration of linear species increases, which can be seen by the broadening of the IR peak and finally the appearance of a second peak close by. The appearance of the polymer could be identified by further broadening in the peak and loss of sharp signals. No general trend regarding temperature (Table 1, Experiment 1–6) and pressure (Table 1, Experiment 1, 7–11) could be identified regarding the formation of the linear species. We therefore assume that the formation of the linear species is mainly dependent on the concentration of styrene oxide, the reaction time, and the catalyst concentration. To further investigate the effect of the bifunctional catalyst, experiments with a broader variation in the catalyst resulted in a different time course of the formation of the cyclic, linear, and polymeric components. Therefore, experiments were carried out in which the amount of one catalyst species was changed (Table 1, Experiments 12–17) and experiments in which the ratio of the catalysts was kept constant, varying the total amount of the bifunctional catalyst (Table 1, Experiments 18–20). It was found that the reaction to cyclic styrene carbonate strongly depends on the correct ratios of the two catalysts, with the total amount of catalyst only influencing the reaction time.

Although we obtain an excess of cyclic carbonate over the reaction time with a lower TBAB concentration, after the end of the reaction, the formation of polymer was nearly constant. For an increased concentration of TBAB, a much faster formation and higher final concentration of the linear carbonate is observed. These studies suggest that the homogeneous reaction pathway is highly sensitive towards different parameters and hardly controllable at a high selectivity for only one product species.

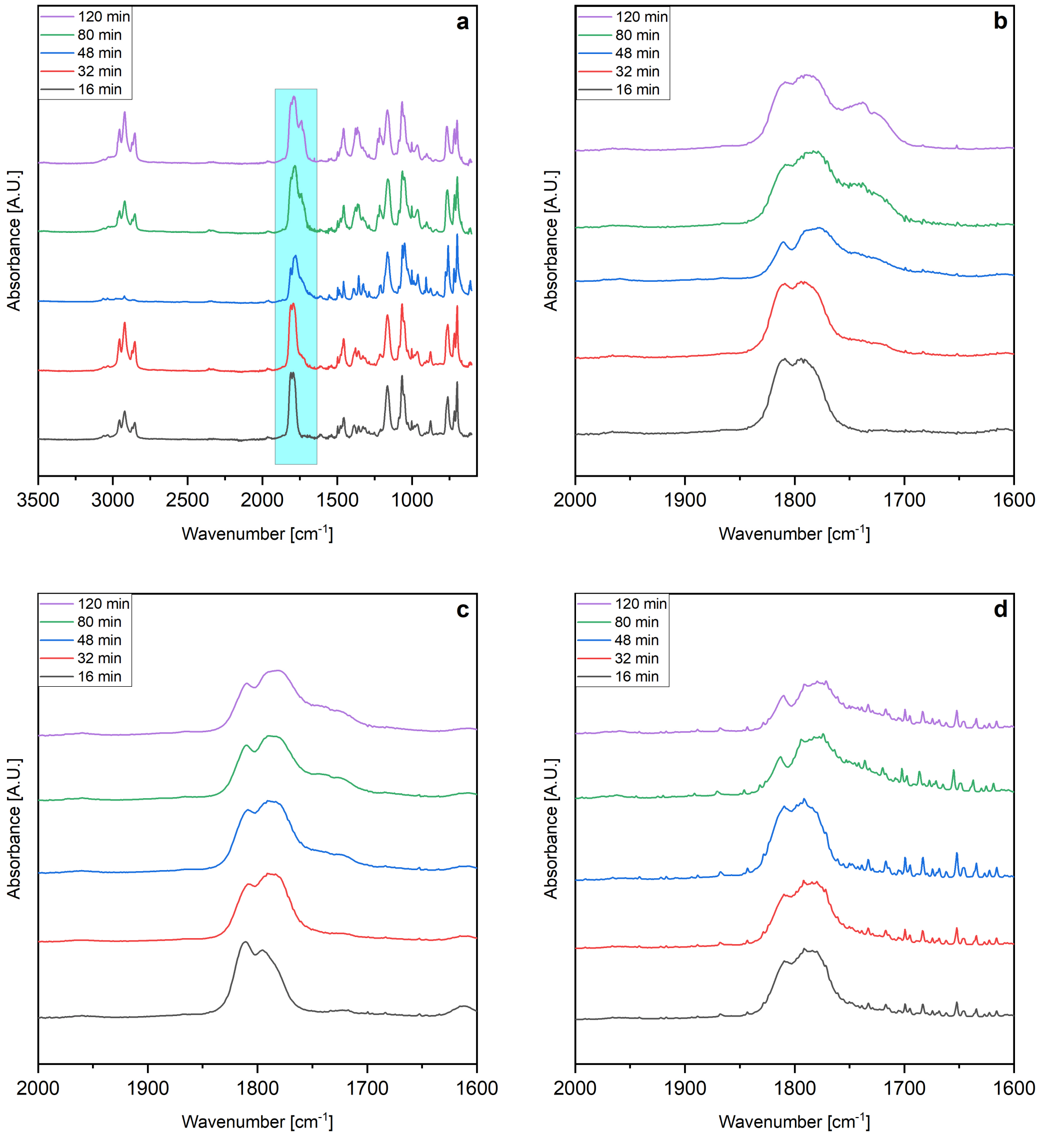

Figure 5. (**a**) ATR-IR spectra of the basic experiment (120 °C, 15 bar), (**b**) resolution change to the relevant peak for the standard reaction, (**c**) ATR-IR spectra for experiment with lower concentration of TBAB, (**d**) ATR-IR spectra for experiment with higher concentration of TBAB.

Experiments with purified cyclic styrene carbonate showed that the cyclic styrene carbonate is surprisingly unstable and can be opened with acetic acid and trigger polymerization. Furthermore, it occurs that manganese dioxide which forms during purification steps after the reaction and deactivation of the catalyst seems to serve as a catalyst for ring-opening polymerization (ROP). As a result of the purification issues of the product as well as the pre-polymerization during the reaction, the products of the autoclave reactions are unsuitable for closer examination of the ROP as pure monomers are required here. For this reason, alternative ways of producing cSC were considered, with organocatalysis being an appropriate approach. Therefore, this was examined more closely, and the products of this reaction were tested for the ROP.

Reference experiments were also carried out with the cobalt-based Jacobsen catalyst (see Table 1, Experiment 21), which is also frequently used in the literature. This catalyst is characterized by a lower price and easier purification. However, the results of these tests correspond to the findings with the manganese-based Jacobsen catalyst in regard of cSC formation. The main difference observed with the cobalt catalyst was a lower reaction rate (see Supplementary Information).

Table 1. Tested experimental conditions to determine the effect of different parameters and calculated yields.

Experiment	Temperature [°C]	Pressure [bar]	Jacobsen Cat. Conc. [mol%]	TBAB Cat. Conc. [mol%]	Y_{SC} [%]	$Y_{Polymer}$ [%]
1	120	15	1	1	72	28
2	114	15	1	1	69	31
3	116	15	1	1	78	22
4	122	15	1	1	88	12
5	128	15	1	1	58	42
6	130	15	1	1	69	31
7	120	10	1	1	75	25
8	120	20	1	1	76	24
9	120	25	1	1	74	26
10	120	30	1	1	81	19
11	120	35	1	1	71	29
12	120	15	0.8	1	74	26
13	120	15	0.6	1	95	5
14	120	15	0.4	1	82	18
15	120	15	1	0.8	58	42
16	120	15	1	0.6	75	25
17	120	15	1	0.4	75	25
18	120	15	0.8	0.8	97	3
19	120	15	0.6	0.6	88	12
20	120	15	0.4	0.4	87	13
21	120	15	1 (JCC)	1	72	28

2.2. *Organocatalytic Synthesis of Styrene Carbonate*

Replication of the work by Baral et al. enabled the synthesis of styrene carbonate and phenol [21]. The direct exchange of diphenyl carbonate with dimethyl carbonate (DMC) under the same reaction conditions resulted in incomplete low conversion around 20–60% (see Table 2, Experiment 22–27). Only experiments with a reaction temperature above 45 °C resulted in a significant conversion with a reaction time of 12 h. A higher DMC content of 3 eq. results in an even higher conversion up to 70–100%, which would indicate an equilibrium (see Table 2, Experiment 28–38, 40). As a validation, the experiment was repeated with 3 eq. DMC and an increased temperature at 65 °C, which corresponds to the boiling point of methanol (see Table 2, Experiment 35). The results of the experiment were analyzed using ATR-IR (see Figure 6) and ^{1}H-NMR, confirming the assumptions (see Figures 7 and 8).

Table 2. Tested experimental conditions to determine the effect of catalyst concentration and reaction temperature.

Experiment	Temperature [°C]	Time [h]	Cat. [mol%]	m_{PED} [g]	m_{DMC} [mL]	Y_{SC} [%]
22	30	3.5	2.0	5.061	2.8	63.99
23	31	4.5	2.0	50.614	28.1	36.10
24	35	3.5	2.0	5.061	2.8	0.00
25	40	3.5	2.0	5.061	2.8	17.35
26	45	3.5	2.0	5.061	2.8	19.65
27	40	3.5	2.0	8.061	2.8	0.00
28	40	12.0	2.0	4.994	13.2	77.79
29	45	12.0	2.0	5.008	13.2	92.56
30	35	12.0	2.0	5.002	14	91.36
31	50	12.0	2.0	5.002	15	93.97

Table 2. *Cont.*

Experiment	Temperature [°C]	Time [h]	Cat. [mol%]	m_{PED} [g]	m_{DMC} [mL]	Y_{SC} [%]
32	10	12.0	2.0	5.008	13	94.51
33	20	12.0	2.0	5.009	13	81.71
34	55	12.0	2.0	5.022	13	97.23
35	60	5.0	2.0	5.075	13	100.00
36	65	4.0	2.0	5.002	13.1	100.00
37	0	12.0	2.0	5.005	13.1	85.57
38	−5	12.0	2.0	5.007	13.1	78.34
39	0	12.0	1.0	5.061	2.8	9.82
40	0	12.0	1.0	5.003	13.1	62.04
41	0	3.5	0.8	5.065	2.8	0.00
42	10	12.0	0.8	5.062	2.8	0.00
43	20	3.5	0.8	5.063	2.8	0.00
44	30	12.0	0.8	5.062	2.8	7.95
45	40	3.5	0.8	5.063	2.8	0.00
46	50	12.0	0.8	5.061	2.8	9.47
47	60	3.5	0.8	5.062	2.8	5.32
48	30	12.0	0.6	5.061	2.8	0.00
49	20	3.5	0.6	5.061	2.8	0.00
50	0	3.5	0.6	5.061	2.8	0.00
51	10	3.5	0.6	5.061	2.8	0.00
52	40	12.0	0.6	5.061	2.8	0.00
53	50	3.5	0.6	5.061	2.8	0.00

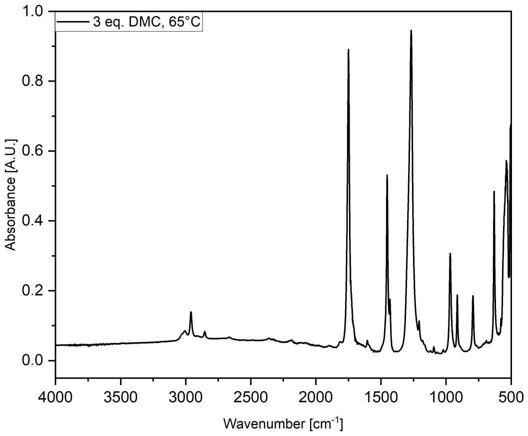

Figure 6. ATR-IR spectrum of the reaction at 3 eq. DMC and 65 °C reaction temperature.

Figure 7 visualizes the signals, mainly due to the protons being close to the carbonyl function. These result in a typical separate cleavage, which makes it possible to determine the yields by NMR. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (m, *J* = 8.6 Hz, ^{1}H), 7.44 (m, *J* = 1.0 Hz, ^{1}H), 7.38 (m, *J* = 2.5 Hz, ^{1}H), 7.36 (m, *J* = 1.8 Hz, ^{1}H), 5.68 (t, *J* = 8.0 Hz, ^{1}H), 4.80 (t, *J* = 8.4 Hz, ^{1}H), 4.35 (dd, *J* = 8.1, 8.5 Hz, ^{1}H).

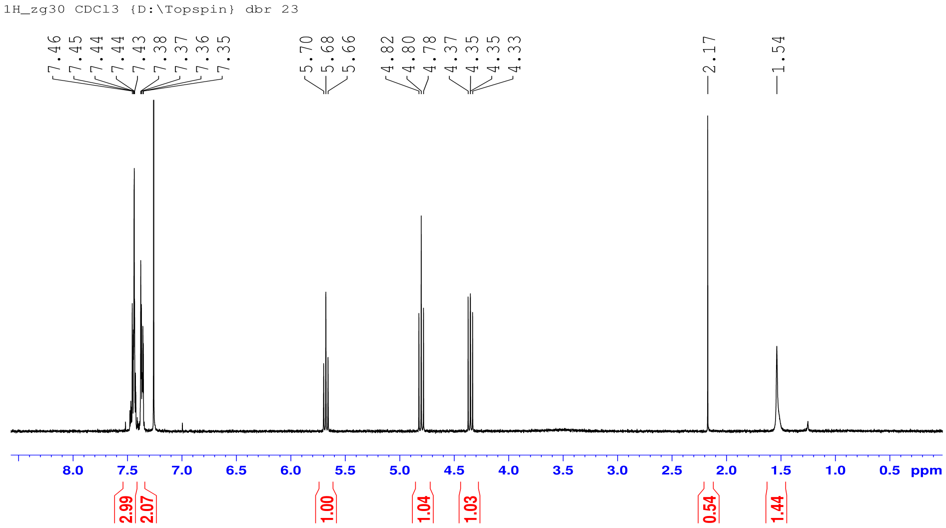

Figure 7. ^{1}H-NMR spectrum styrene carbonate reference substance purchased from Sigma Aldrich (Saint Louis, MO, USA).

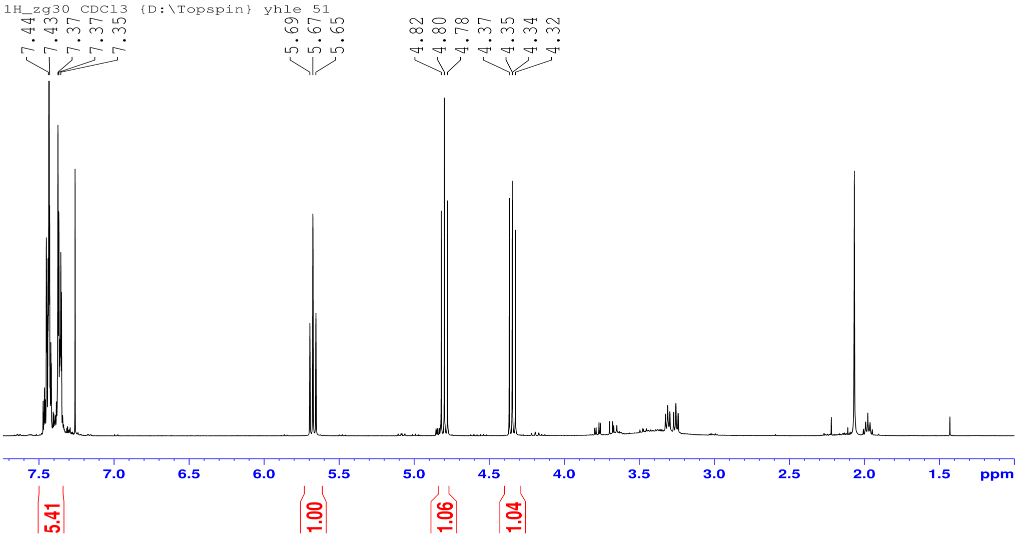

Figure 8. ^{1}H-NMR spectrum of styrene carbonate of the reaction at 3 eq. DMC and 65 °C reaction temperature.

The ^{1}H-NMR spectrum of the sample (see Figure 8) corresponds to the reference spectrum; a styrene carbonate reference substance purchased from Sigma Aldrich (see Figure 7). Figure 8 shows that almost no traces of PED are visible and therefore a complete conversion has taken place. The experiment also shows that an excess of DMC is necessary to achieve high conversion rates (see Table 2, Experiment 24–27, 41–53) and demonstrated a high reproducibility. A further investigation of the reaction temperature range revealed a complete conversion only at temperatures below $-10°$. These results correspond to the expectations for an exothermic equilibrium in the reaction of DMC with PED. In general, a high selectivity of the reaction was observed. HPLC analyses showed that no by-products were formed (see Figure 9) and only reactant residues were detected. These could be easily removed by extraction with dichloromethane.

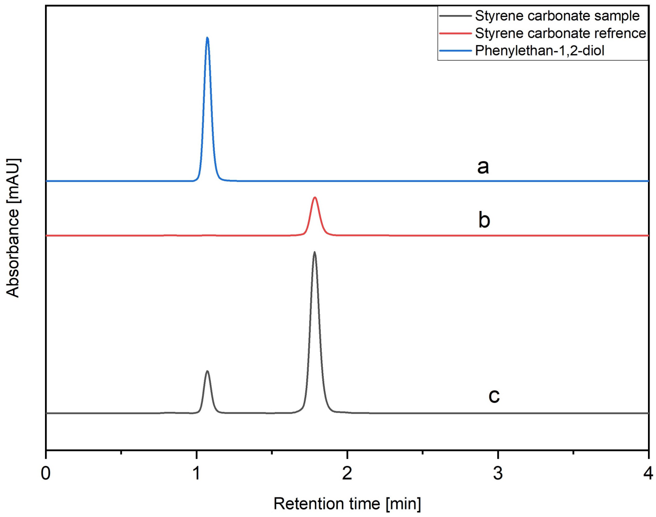

Figure 9. (**a**) HPLC-DAD chromatogram of the starting material phenylethane-1,2-diol. (**b**) HPLC-DAD chromatogram of the styrene carbonate reference substance, obtained from Sigma Aldrich. (**c**) HPLC-DAD chromatogram of the styrene carbonate produced from the organocatalytic production of styrene carbonate.

The following optimum conditions were determined for the synthesis of styrene carbonate. The temperature to obtain the highest yield of styrene carbonate is 65 °C with a catalyst amount of 2 mol%.

2.3. Ring Opening Polymerization Test of Cyclic Styrene Carbonate

In order to investigate the suitability of the purified cyclic styrene carbonate (cSC) from the organocatalytic experiments, ring-opening polymerization (ROP) experiments were performed. This product could be utilized, since the organocatalytic product contains only product and reactant, which itself functions as a starter (see Figure 9). The experiments were carried out in batch mode, which guranteed a high conversion and high molar mass of the polymer, monitored using an in situ IR probe (see Figure 10).

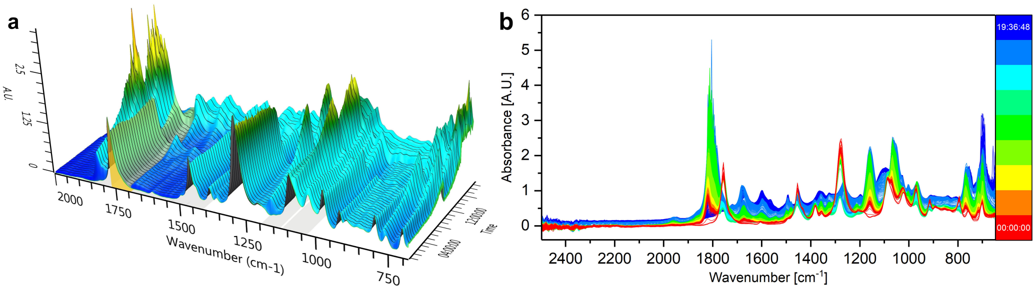

Figure 10. (**a**) Recording of the probe ATR-IR spectrum during the formation of cSC with subsequent ROP. (**b**) Chronological view with focus on the changing bands of the ATR IR spectrum during the formation of cyclic styrene carbonate with subsequent ROP.

The cyclic styrene carbonate (∼1800 cm^{-1}) was formed over 14 h in 2-Me-THF. Subsequently, the solvent was removed (∼1200 cm^{-1}), phenylacetic acid was added as a starter to initiate the reaction mixture at 160 °C to initialize the ROP. This results in the formation of dark-brown transparent polymeric solids. The resulting samples were analyzed using DSC, where one exothermic peak for the glass temperature was detected at 160 °C and one endothermic peak at 185 °C which corresponds to the melting point (see Figure 11).

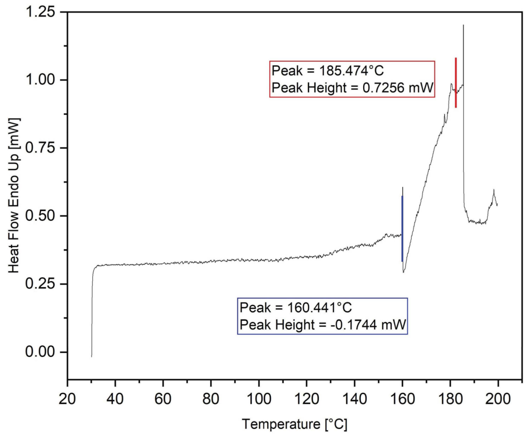

Figure 11. DSC spectrum of the products of the ROP of styrene carbonate.

The samples were also analyzed using TGA, which revealed a significant decomposition of the product at temperatures above 220–240 °C. Measurements using HPLC-ESI-MS revealed a molar mass above 44 kDa. Measurements of viscosity to determine the molar mass based on the data from Kulicke et al. [42] were made by measuring the viscosity of a 3% solution in toluene. A molar mass of 48,000 g/mol was determined via the measurement of the viscosity.

3. Materials and Methods

3.1. Chemicals Used and Suppliers

The following chemicals with the indicated purities were used for the experiments. (*R*,*R*)-(-)-*N*,*N*′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobald(II) (JCC, 98%), 1-Phenyl-1,2-ethandiol (PED, 97%), (*R*,*R*)-(-)-*N*,*N*′-Bis(3,5-di-tert-butylsalicyliden)-1,2-cyclohexandiaminomangan(III)-chlorid (JCM, 96%), Styrene oxide (SO, 97%), and Tetrabutyl ammonium bromide (TBAB, 99%) were obtained from Thermo Fisher Scientific (Henningsdorf, Germany). Methanol (99.9%) was obtained from VWR (Dresden, Germany). Dichlormethan-D2 (99.5%), Tichlormethan-D1 (99.8%), Dimethyl carbonate (DMC, 99.8%), Diphenyl carbonate (DPC, 99%), 2 Methyltertahydrofuran (2-Me-THF, 99%), n-Heptan (99%), n-Hexan (99%), and n-Octan (99%) were obtained from Roth (Karlsruhe, Germany). 1,5,7-Triazabicyclo[4.4.0]dec-5-en (TBD, 98%) and Styrene carbonate (cSC, 99%) were obtained from Sigma Aldrich (St. Louis, MO, USA).

3.2. Experimentel Section

In this work, the synthesis of styrene carbonate was studied under homogenous and organocatalytic conditions from different precursors based on styrene derivatives. As part of this research, the experimental parameters were selectively varied to investigate the influence of the individual parameters on the respective methods.

3.2.1. Conditions for High-Pressure Homogeneous Catalytic Synthesis

The homogeneous synthesis of styrene carbonate is based on the work of Balas et al. [11] and was performed in a high-velocity stirred stainless-steel autoclave with a Teflon inlet (50 mL) which is pressure and temperature controlled (see Figure 12).

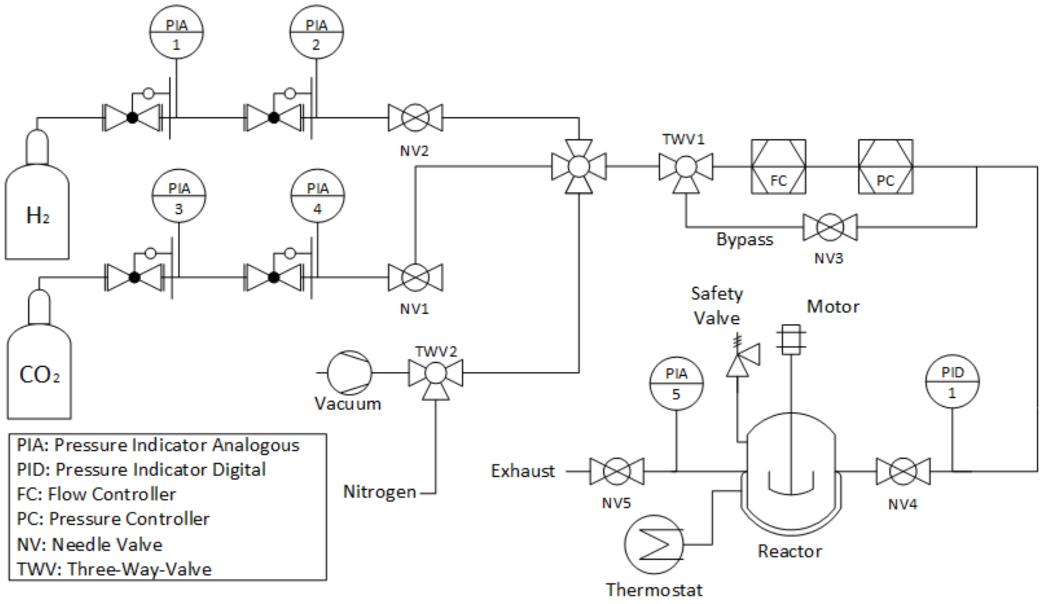

Figure 12. Reaction setup for the high-pressure homogeneous synthesis of styrene carbonate.

In a typical experiment, Tetrabutyl ammonium bromide (TBAB, 1 mol%) and the manganese Jacobsen catalyst (JCM, 1 mol%) were dissolved in n-Octan (13.3 mL). To this mixture, Styrene oxide (SO, 6.1 mmol) was added. The reaction mixture was then flushed with nitrogen and stirred for 10 min. To remove dissolved gases, it was evacuated afterward. The reactor was heated to the respective reaction temperature and pressurized with CO_2 to the respective pressure (see Table 1) which initiated the start of the reaction. Through the usage of a combination of a pressure sensor and a mass flow controller, the pressure was constantly monitored and kept constant at its set point. The total conversion of the reaction was monitored through the gas flow volume of CO_2. The yield of the carbonate and polymer was calculated from the CO_2 consumption (see Table 1), where no clear distinction could be made between linear and cyclic carbonate. For selected experiments, the progress was followed by collecting samples over the reaction time analyzed by ^{1}H-NMR (400 Hz) and ATR-IR.

3.2.2. Conditions for Organocatalytic Synthesis

The synthesis is based on the work of Baral et al. [21] where diphenyl carbonate (DPC) was used as a reagent. DPC (1.1 eq.) and 1-phenyl-1,2-ethanediol (PED, 1 eq.), were dissolved in 2-Me-THF and placed in the reactor. The catalyst 1,5,7-Triazabicyclo[4.4.0]dec-5-en (TBD, 2 mol%) was added after the reactor was flushed with nitrogen gas (N_2), as the catalyst is sensitive to moisture. The reaction was thermostated to 40 °C and after 6 h the reaction was quenched by the addition of acetic acid (AcOH, 10 mL) until the pH value was fully acidic. The solvent was removed from the reaction mixture by a rotary evaporator at 60 °C and a pressure of 400 mbar to 23 mbar. The product was analyzed by ^{1}H-NMR (400 Hz). The results show that styrene carbonate was obtained at a high conversion of the starting material PED. However, the product is mixed with phenol which is difficult to remove. Based on this observation, DPC was replaced by an alternative carbonate source, dimethyl carbonate (DMC, 1.1 eq.), as this releases methanol as a reaction product, which can be easily removed, e.g., using rotary evaporators (see Figure 13).

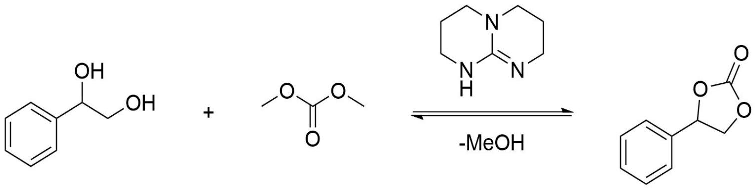

Figure 13. Synthesis of cyclic styrene carbonate by reaction of phenyl ethanediol with dimethyl carbonate.

The experimental setup shown in Figure 14 was used for the organocatalytic synthesis of styrene carbonate. This setup enables easy multigram (20–100 g) access to styrene carbonate.

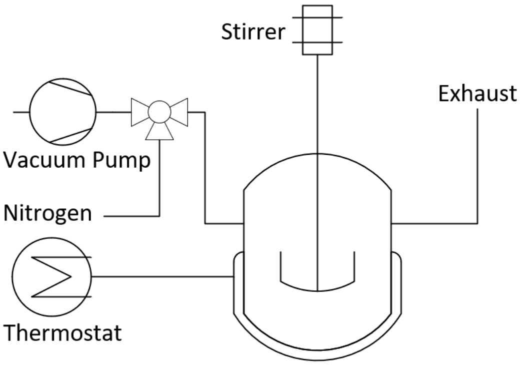

Figure 14. Experimental setup for the organocatalytic synthesis of styrene carbonate.

The reaction was performed at different temperatures and concentrations of dimethyl carbonate and catalyst in a test series based on the above-mentioned experimental parameters. The exact test parameters are summarized in Table 2. Conversion rates in Table 2 are determined by the ratios of the area integrals of the ^{1}H-NMR spectra (see Supporting Information Figures S1–S32).

3.2.3. Ring-Opening Polymerization

In order to test the suitability of the resulting cyclic styrene carbonate for ring-opening polymerization (ROP), experiments were performed with TBD proposed by Brüggemann et al. and Mojgan et al. [7,8]. The reaction conditions employed were 0.01 eq. catalyst and 0.05 eq. phenylacetic acid as starter at 160 °C reaction temperature. The synthesis path is illustrated in Figure 15.

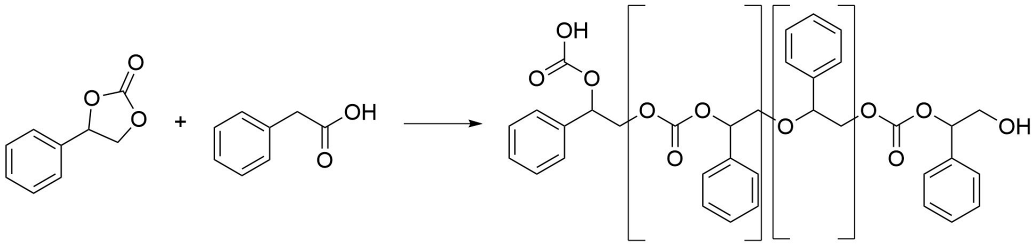

Figure 15. Synthesis of Polystyrene carbonate by ROP of styrene carbonate with phenylacetic acid.

The reactions were performed using a 50 mL reactor with a heatable jacket. The reactor has a GL25 opening for an in situ IR probe and two feed valves for operation under inert gas. The reactor was heated by a Haake F6 thermostat. Silicone oil AP200 was chosen as the operating fluid for the thermostat. The IKA RCT Basic magnetic stirrer (IKA-Werke GmbH und CO. KG, Staufen, Germany) was used for mixing. A Mettler Toledo Reakt IR 15 (Mettler Toledo GmbH, Gießen, Germany) was used for the in situ measurements. The spectrometer is equipped with a Si probe, connected to the spectrometer via AgX

9.5 mm × 1.5 mm fiber optics. The measured wavenumber range is from 4000 cm^{-1} to 800 cm^{-1} with a resolution of 4 cm^{-1}.

3.3. Analytical Methods

All samples were analyzed after synthesis by ATR-IR in the range of 600–4000 cm^{-1} with 128 scans and a resolution of 1 cm^{-1}. Furthermore, samples (100 µL sample diluted in 1.5 mL Water:Acetonirile (40:60)) were measured via HPLC-ESI-DAD equipped with an ISASPHERE 1005 C18 BDS Column, with an oven temperature of 30 °C and a flowrate of 1 $\frac{mL}{min}$. The runtime per experiment was 20 min with an eluent composition of 0.01% acetic acid in water (A): acetonitrile (B) in a ratio 40:60 (A:B). The DAD was set on 254 and 225 nm with a bandwidth of 2 nm. The ESI-detector evaporator temperature was set at 25 °C with a nebulizer temperature of 35 °C. A carrier gas flow rate of nitrogen with 1.60 SLM was set.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Teller Pyris DSC-6 in Perkin Elmer stainless steel capsules with a capacity of 60 µL. Measurements were carried out from 30 °C to 200 °C with a heating rate of 1 $\frac{K}{min}$ under nitrogen atmosphere (nitrogen flow rate = 60 $\frac{mL}{min}$).

^{1}H-NMR and ^{13}C-NMR were measured in a Norell 502 on a Bruker Advance II (Bruker, Billerica, MA, USA) 400 MHz with a DUL 5 mm double resonance probe (^{1}H, ^{13}C, Z-gradient, ATM). For sample preparation, a spatula tip of the sample was mixed with 600 µL Chloroform-D1 or Dichlormethan-D2. The solvent was selected based on the respective sample matrix.

4. Conclusions

In the scope of this work, some valuable findings could be collected, as the simplest method to produce highly pure styrene carbonate is the conversion of DMC and PED at 65 °C using an organocatalyst. This organocatalytic reaction of PED with DMC results in an equilibrium that can best be controlled by removing the produced methanol.

The observed complexity of the homogeneous autoclave reaction requires a deeper analysis using theoretical approaches and kinetics. However, it could be demonstrated that this is an example of bifunctional catalysis with the potential to control the course of the reaction by tuning the catalyst composition. Through online-ATR-IR analyses during the reaction, it was also possible to determine that cyclic styrene carbonate always forms first and that linear polymer styrene carbonate forms first during the reaction. This corresponds to an end-of-life problem. During the reaction, the fraction of cSC increases more and more. In addition, cSC is relatively unstable, and the ring can easily be opened, e.g., by bases such as TBAT or simple acetic acid. This leads to the linear styrene carbonate on the catalyst having an increasingly higher chance of undergoing a ring-opening polymerization during the reaction, as already proposed by Brüggemann et al. [8].

This also clarifies the hen–egg problem of quite a lot of current literature on the synthesis of polystyrene carbonate, where it is unclear whether the cSC is a by-product of the polymerization reaction or a consecutive product, generated by backbiting. The findings of this work are much more in favor of the formation of cSC as the primary product which then undergoes ROP when it is kinetically favored by the concentration of reactants and intermediates in the reaction mixture.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal14060362/s1. Table S1 of the Supporting Information shows all experiments of organo-catalysis of styrene carbonate and the corresponding images of the 1H-NMR data. Figures S1–S32 show the corresponding NMR spectra. Figure S33 shows the visible difference between cyclic carbonate and polymerized species from the autoclave experiments. Figure S34 shows the CO_2 consumption for the diffrent Jacobsen catalysts.

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Conflicts of Interest: Author Daniel Brüggemann was employed by the company Covestro Deutschland AG, Leverkusen, Germany. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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