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ARTICLE

Synthesis of high-molecular-weight aliphatic polycarbonates by organo-catalysis

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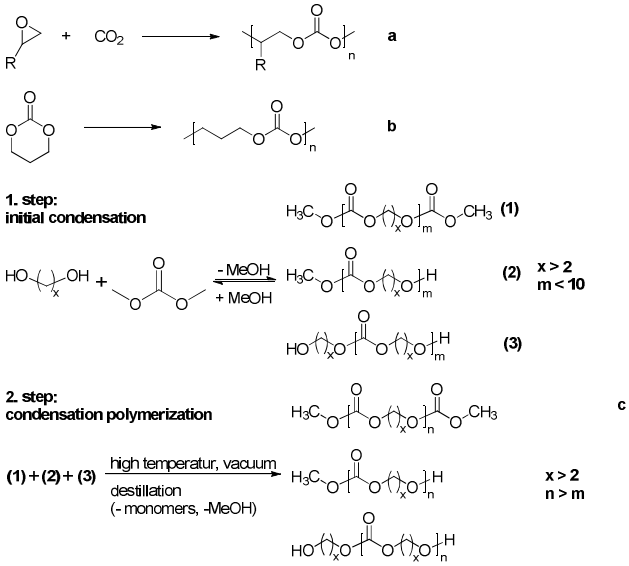
Aliphatic polycarbonates attract significant attention for biomedical application during last years due to their biodegradability, low toxicity and good biocompatibility. However, in most cases, the use of metal-based catalysts is required for the preparation of aliphatic polycarbonates by the polycondensation method, which is difficult to remove completely from the final polymer. For this reason, our work is focused on the synthesis of high-molecular-weight aliphatic polycarbonates using organo-catalysts via a two-step polycondensation of dimethyl carbonate and a linear alkane diol as monomers. A variety of organo-catalysts has been surveyed for the synthesis of aliphatic polycarbonates. The influence of thiourea with mono- or bi- electron acceptor groups as cocatalyst, which was found to activate the carbonyl groups of lactide and trimethylene carbonate in the ring opening polymerization successfully, was investigated in the polycondensation. In summary high-molecular-weight aliphatic polycarbonates, such as poly(1,4-butylene carbonate) (PBC), poly(1,5-pentamethylene carbonate) (PPC) and poly(1,6-hexamethylene carbonate) (PHC), were successfully prepared with number averaged molar mass (M_n) up to 23000 g/mol, dispersities below 1.8 and high yield of > 80 % under relatively mild operating conditions (T < 130 °C) using 4-dimethylaminopyridine (DMAP) as catalyst. At 170 °C the poly(1,4-butylene carbonate) with M_n of 52000 g/mol was synthesized. Additionally, hydroxyl group terminated poly(1,4-butylene carbonate) with M_n up to 17000 g/mol were obtained and characterized with ^{1}H NMR spectroscopy and ESI-ToF-mass spectrometry. The ratio of end groups (-OH/-OC(O)O-CH_3) could be adjusted by using different feed ratio or catalysts.

Introduction

Polycarbonates (PCs) are polymers containing repeating carbonate groups (-O-(C=O)-O-). Aromatic polycarbonates are widely used as engineering plastics[1,2] because of their attractive mechanical properties, e.g. low moisture absorption, high impact strength, high elastic modulus, creep resistance and good thermal stability. However, compared with traditional aromatic polycarbonates aliphatic polycarbonates received little interest because of their poor thermal stability and high susceptibility to hydrolysis.[1,3–7] During last years aliphatic polycarbonates attract significantly increasing attention for biomedical application, e.g. for the composition of biomedical implants and acting as drug delivery device, due to their biodegradability, low toxicity and good biocompatibility.[1,4,8–11] Aliphatic polycarbonates can be prepared through different methods, such as copolymerization of CO_2 and an epoxide (Scheme 1a)[12,13], which is only suitable for the synthesis of aliphatic polycarbonates in which the carbonate linkages are connected by two carbon atoms, ring opening polymerization of cyclic carbonate monomers (Scheme 1b)[1,14–18] and condensation polymerization of dialkyl- or diphenyl carbonate and aliphatic diols (Scheme 1c).[4,19–26]



Scheme 1. Various methods for preparation of aliphatic polycarbonates

The ring opening polymerization of cyclic carbonates is one of the most effective method to obtain polycarbonates with high molar

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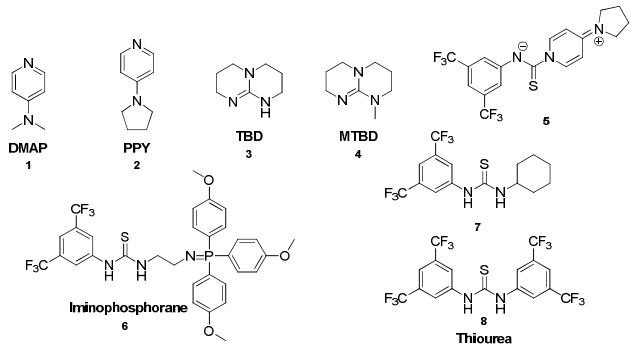


Scheme 2. Organo-catalysts for synthesis of aliphatic polycarbonate via polycondensation method

mass and low dispersity.[20] However, cyclic carbonate monomers arevery expensive because of their low synthetic yields. Hence, polycarbonates from ring opening polymerization have been mainly investigated for biomedical application.[22,27,28] The best strategy for large-scale preparation of aliphatic polycarbonates is the two-step condensation polymerization of dimethyl carbonate (DMC) and aliphatic diols with more than three carbon atoms. Oligomers with molar mass lower than 1000 g/mol are obtained in the first, initial condensation step, due to the low equilibrium constant. In the second step, polymer chains propagate by transesterification between the hydroxyl and methyl carbonate or two methyl carbonate end groups in the presence of transesterification catalysts, while high temperature and high vacuum are required to remove unreacted monomers and freshly generated byproducts. The resulting oligomers or polymers have three possible end group compositions, hydroxyl end groups, methyl carbonate end groups or a combination of both (Scheme 1c).[19, 20, 22] Recently, Li et al. reported the preparation of polycarbonates with high molar mass (M_n up to 94000 g/mol) using a novel TiO_2/SiO_2-poly(vinyl pyrrolidone)-based catalyst (TSP-44).[21] Lee et al. has used NaH as catalyst to prepare aliphatic polycarbonate with high molar mass (M_n up to 150000 g/mol) successfully with the prerequisite that the [-OH]/[-OCH_3] ratio of the oligomers generated in the transesterification step is about 1.0.[22] However, in most cases, the use of metal-based catalysts is required for the preparation of aliphatic polycarbonates by the polycondensation method, which is difficult to remove completely from the final polymer.

For this reason our work is focused on the synthesis of high-molecular-weight polycarbonates using organo-catalysts via a two-step polycondensation of dimethyl carbonate and a linear alkane diol as monomers. Some organo-catalysts such as guanidines, amidine and tertiary amines have been used in the ring opening polymerization of trimethylene carbonate (TMC) and shown to yield poly(trimethylene carbonate) with high molar mass (M_n up to 72000 g/mol), with low dispersities ($Đ_M$ = 1.04 - 1.80) and with well-defined terminal groups.[15,16,29] Furthermore, thiourea derivates have been reported for the direct activation of electrophilic substrates via employment of double hydrogen bonding. Hedrick[30,31] and Dioxon[32] demonstrated that thiourea based bifunctional organo-catalyst effectively activated the ring opening polymerization of cyclic esters. Moreover, Hedrick reported that electrophilic thioureas and nucleophilic bases are not required to be linked in the same molecule.[31] Kosugi has exploited a 3,5-bis(trifluromethyl)phenyl and 4-pyrrolidinopyridine (PPY) based zwitter ionic salt organo-catalyst for transesterification reactions.[33] However, there have been few reports about the successful synthesis of aliphatic polycarbonate with high-molecular-weight using organo-catalysts through condensation polymerization of DMC and diols. Picquet and Plasseraud described a route to the synthesis of aliphatic polycarbonates (M_n up to 7400 g/mol) using 1-*n*-butyl-3-methylimidazol-2-carboxylate (BMIM-2-CO_2) as catalyst.[4]

In this work, a variety of organo-catalysts (Scheme 2) has been surveyed for the synthesis of aliphatic polycarbonates. The influence of thiourea with mono- or bi-electron acceptor groups as cocatatlyst, which were found to activate the carbonyl groups of lactide and trimethylene carbonate in the ring opening polymerization successfully, was investigated in the polycondensation as well.

Experimental

Materials

1,4-Butane diol (99+ %) was purchased from Acros Organics and vacuum distilled using a short path distillation apparatus and dried with 4 Å molecular sieve before use. Other diols (C > 4) were dried under vacuum at ambient temperature over night before use. The arylaminothiocarbonylpyridinium salt (5)[33], bifunctional iminophosphorane (6)[32] and thioureas (7 and 8)[34] catalysts were synthesized as previously reported. Other Reagents were available commercially and used as received.

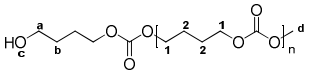
Measurements

^{1}H and ^{13}C NMR spectra were obtained using Bruker AV 500 spectrometer at 500 MHz and 125 MHz, respectively. Chloroform-*d* ($CDCl_3$, 99.8 D%), dimethylsulfoxide-d_6 (DMSO-d_6, 99.5 D%) or acetonenitrile-d_3 (MeCN-d_3, 99 D%) were used as solvent for NMR measurements. The molar masses and molar mass distribution (M_w/M_n) were analyzed employing size exclusion chromatography (SEC) system equipped with four consecutive columns (PSS-SDV columns filled with 5 µm gel particles with a defined porosity of 10^6 Å, 10^4 Å, 10^3 Å and 10^2 Å, respectively) and a Shodex RI-detector (RI-101) at 30 °C. The system was operated at a flow of 0.75 mL/min with chloroform as solvent. Polystyrene standards were used for calibration.

ESI-ToF-mass spectra in the m/z range 400 - 4000 were measured on a SYNAPT ^{TM} G2 HDMS ^{TM} from Waters. The mass spectrometric parameters were the following: Capillary voltage: 2.5 kV; sampling cone voltage: 50 V; extraction cone voltage: 1V; cone gas flow: 30 L/h; source temperature: 120 °C; desolvation gas flow: 650 L/h; desolvation temperature: 350 °C; helium cell gas flow: 180 mL/min; IMS gas flow: 90 mL/min; IMS wave velocity: 460 m/s; IMS wave height: 40 V. The PBC sample was dissolved in acetonitrile (2 g/L) and then mixed with NaI 0.1 g/L in methanol and methanol in the ratio of 5 : 5 : 990. Data were obtained and processed using Drift Scope 2.4 and Polymerix Software.

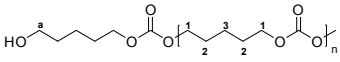
General procedure for condensation polymerization of diols and DMC

In a two-necked flask connected to a Schlenk line with vacuum and argon gas lines diol, DMC and organic catalysts were added under argon atmosphere. The mixture was stirred in an oil bath at 130 °C until achieving the equilibrium determinated by ^{1}H NMR spectroscopy within 2 - 18 h. Before starting the second step, the flask was equipped with a vacuum distillation apparatus. In the second step the condensation polymerization was carried out under reduced pressure with the oil bath temperature maintained at 130 °C or increased to 170 °C. The condensation polymerization was conducted over night. The mixture was then cooled to room temperature and dissolved in chloroform. The polymer was isolated by precipitation in ethanol and dried under vacuum to give a white solid.



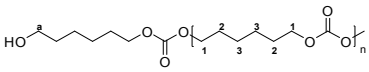
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.65 (m, 3 H, $^bCH_2$, ^cOH), 1.76 (b, 4 H, $^2CH_2$), 3.68 (t, 2 H, J_{HH} = 6.3 Hz, $^aCH_2$), 3.77 (s, 3 H, O^dCH_3), 4.15 (b, 4 H, $^1CH_2$)



^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.46 (m, 2 H, $^3CH_2$), 1.70 (m, 4 H, $^2CH_2$), 3.65 (t, 2 H, J_{HH} = 6.5 Hz, $^aCH_2$), 3.77 (s, 3 H, O^bCH_3), 4.13 (t, 4 H, J_{HH} = 6.6 Hz, $^1CH_2$)



^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.40 (m, 4 H, $^3CH_2$), 1.67 (m, 4 H, $^2CH_2$), 3.63 (t, 2 H, J_{HH} = 6.5 Hz, $^aCH_2$), 3.76 (s, 3 H, O^bCH_3), 4.11 (t, 4 H, J_{HH} = 6.8 Hz, $^1CH_2$)

Results and discussion

Catalyst Screening

A variety of organo-catalysts such as commercially available pyridines (4-dimethylaminopyridine, DMAP (**1**) and 4-pyrrolidinopyridine, PPY (**2**)), guanidines (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD (**3**) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, MTBD (**4**)), bifunctional arylaminothiocarbonylpyridinium salt (**5**) and iminophosphorane (**6**) have been used in the condensation polymerization of diols and dimethyl carbonate (DMC). Furthermore, the 4-dimethylaminopyridine (**1**) was also investigated together with thioureas with mono- (**7**) and bi- (**8**) electron withdrawing 3,5-bis(trifluromethyl)phenyl groups as cocatalyst. Such compounds were used in the ring opening polymerization of trimethylene carbonate successfully,[15,16,30] and it was of interest to test the influence of thiourea in the transesterification step and in the condensation polymerization. In the first step the transesterification reaction of DMC and diol is an equilibrium reaction. According to the Le Chatelier's principle the chemical

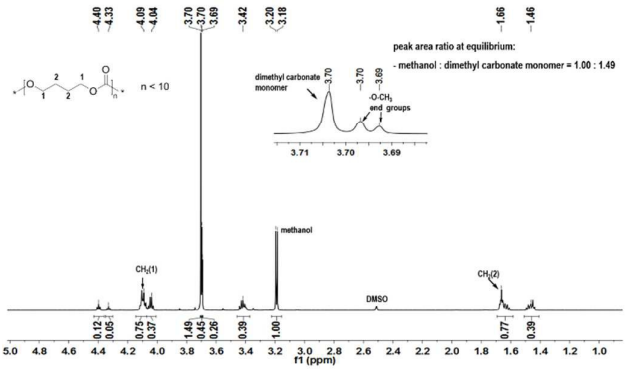
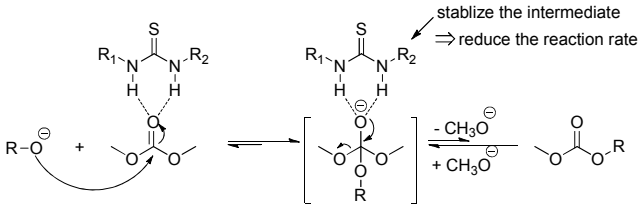


Figure 1. ^{1}H NMR spectrum of the reaction solution of BD and DMC using cat. 1 at equilibrium



Scheme 3. Possible mechanism of thioureas catalyzed transesterification reaction

equilibrium could only be affected by change in temperature or feed ratio. At the equilibrium point the conversions of -CH_2OH to -CH_2OC(O)O-groups should be constant, which is shown in ^{1}H NMR spectrum of the reaction solution at this point as constant peak area ratio of unreacted dimethyl carbonate (3.70 ppm in DMSO-d_6) and generated byproduct methanol (3,19 ppm in DMSO-d_6). (Figure 1)

The catalytic activities of various organo-catalyst systems with respect to the transesterification step of 1,4-butanediol (BD) and DMC were evaluated by comparing the necessary time to achieve the equilibrium. The fewer time the system needed, the higher the activity of the system. Table 1 summarizes the results of the different catalyst systems in the transesterification step under argon atmosphere with a constant feed ratio of [BD] : [DMC] : [cat.] = 1 : 1.2 : 0.005 at 130 °C.

All catalyst systems investigated were active for the transesterification of BD and DMC. It was found that the transesterification reaction was carried out readily (< 1 h) in the presence of pyridine (cat. 3 and 4) and guanidine (cat. 5 and 6) catalysts. However the same reaction catalyzed either by bifunctional catalysts including thioureas groups (cat. 1 and 2) or by DMAP with mono- or bi- electron withdrawing 3,5-bis(trifluromethyl)phenyl groups thiourea (cat. 7 and 8) cocatalysts proceeded much slower.

A proposed mechanism is shown in scheme 3. The thiourea is able for the direct activation of the carbonyl group by means of double hydrogen bonding. The activation may lead to a more stable intermediate, which may subsequently release the methanol difficultly. This also indicates why the thiourea based catalysts could

be used in the ring opening polymerization of cyclic ester or carbonates and inhibiting simultaneously the transesterification side reaction.

Table 1. Catalyst screening of condensation polymerization of BD and DMC

entry	catalyst systems	time to achieve equilibrium[1]	M_n[2] (g/mol)	$Đ_M$[2]
1	cat. 1	1.0 h	16000	1.66
2	cat. 2	1.0 h	7900	2.03
3	cat. 3	0.5 h	6200	2.18
4	cat. 4	< 0.5 h	17000	1.77
5	cat. 5	3.0 h	4100	2.40
6	cat. 6	over night	13000	1.68
7	cat. 4 + cat. 7	2.5 h	6900	2.16
8	cat. 4 + cat. 8	3.0 h	7500	1.80

BD : DMC : cat. = 1 : 1.2 : 0.005
Reaction time:
1. step: until equilibrium
2. step: over night
[1] determined using ^{1}H NMR spectroscopy
[2] determined using SEC in chloroform with PS standards

Besides the transesterification step all catalyst systems were also investigated in the polymerization step after achieving the equilibrium in the 1. step. All catalyst systems were effective for the synthesis of poly(butylene carbonate) from BD and DMC and polycarbonates were obtained with molar masses higher than 4100 g/mol and dispersities lower than 2.40. DMAP (cat. 1) and MTBD (cat. 4) showed the best results with the synthesized polycarbonate having a molar mass up to 17000 g/mol and dispersity of 1.66. Also in polycondensation step, thioureas as cocatalyst retarded the polymerization. Moreover, an experiment without any catalyst was also evaluated at 130 °C and 170 °C for 1. and 2. steps, respectively. However, the ^{1}H NMR spectrum after first step showed, that the transesterification reaction between DMC and BD did not occur. All of compounds in the reaction flask were distilled off after 30 min in the second step. That proved also the efficiency of all investigated catalyst systems.

Results of polycarbonate synthesis

The polymerization temperature and initial feed ratio of diol and DMC are further two important parameters. They can influence the final polymer properties significantly. In order to obtain polycarbonates with higher molar mass we optimized the polymerization conditions. The initial [BD] : [DMC] ratio was varied from 1 : 1.2 up to 1 : 2.0 and the temperatures in condensation polymerization step was set from 130 °C up to 170 °C. The aim of using excess dimethyl carbonate is enhancing the conversion of diols in the 1. step and obtaining oligomers with more methyl carbonate end group, which is more reactive than hydroxyl end group in the 2. step for transesterification reaction between two polymer chains and thus leading to higher molar masses. Excess of DMC was removed in the 2. step.[24]

Table 2 summarizes the most significant results of the polycarbonate synthesis under different polymerization conditions. As shown M_n increased significantly from 5900 g/mol to 11000 g/mol, respectively, while the feed ratio changed from 1 : 1.5 : 0.5 mol-% to 1 : 2.0 : 1 mol-% (entry 1 - 3). Indicating that the methyl carbonate end group is more reactive than the hydroxyl end group in the condensation polymerization step. With the feed ratio of 1 : 2.0 : 1 mol-% PBC, PPC and PHC samples with relatively high M_n values up to 23000 g/mol were obtained in the presence of more reactive catalyst DMAP (entry 9, 11 and 12). Yields were achieved up to 88 %, which was calculated by the following equation (Eq. 1).

$$\text{Yield} = \frac{\frac{mass\ of\ purified\ polymer}{molecular\ weight\ of\ repeating\ unit}}{mole\ of\ diol} \times 100\ \% \qquad \text{(Eq. 1)}$$

whereby 116 g/mol, 128 g/mol and 140 g/mol are the molar mass of repeating units for PBC, PPC and PHC, respectively. Moreover, M_n values increased with increasing temperature from 130 °C to 170 °C (entry 9 and 10).

Table 2. Results of polycarbonate synthesis

	[diol]:[DMC]:[cat.]	Cat.	T (2. step) (°C)	Yields (%)	M_n[1] (g/mol)	$Đ_M$[1]	End groups[2] [-OCH_3]:[-OH]
PBC 1	1 : 1.5 : 0.005	cat. 5	130	60	5900	1.85	2: 98
PBC 2	1 : 1.5 : 0.01	cat. 5	130	70	9000	1.69	14 : 86
PBC 3	1 : 2.0 : 0.01	cat. 5	130	65	11000	1.71	80 : 20
PBC 4	1 : 1.2 : 0.005	cat. 1	130	57	16000	1.66	0 : 100
PBC 5	1 : 1.2 : 0.005	cat. 2	130	59	7900	2.03	0 : 100
PBC 6	1 : 1.2 : 0.005	cat. 4	130	61	17000	1.77	0 : 100
PBC 7	1 : 1.2 : 0.005	cat. 5	130	57	4100	2.40	0 : 100
PBC 8	1 : 1.2 : 0.005	cat. 6	130	53	13000	1.68	0 : 100
PBC 9	1 : 2.0 : 0.01	cat. 1	130	85	23000	1.77	32 : 68
PBC 10	1 : 2.0 : 0.01	cat. 1	170	79	52000	1.77	70 : 30
PPC 1	1 : 2.0 : 0.01	cat. 1	130	77	22000	1.60	43 : 57
PHC 1	1 : 2.0 : 0.01	cat. 1	130	88	23000	1.53	61 : 39

[1] determined using SEC in chloroform with PS standards
[2] determined using ^{1}H NMR spectroscopy

Reaction time:

1. step: until equilibrium
2. step: over night

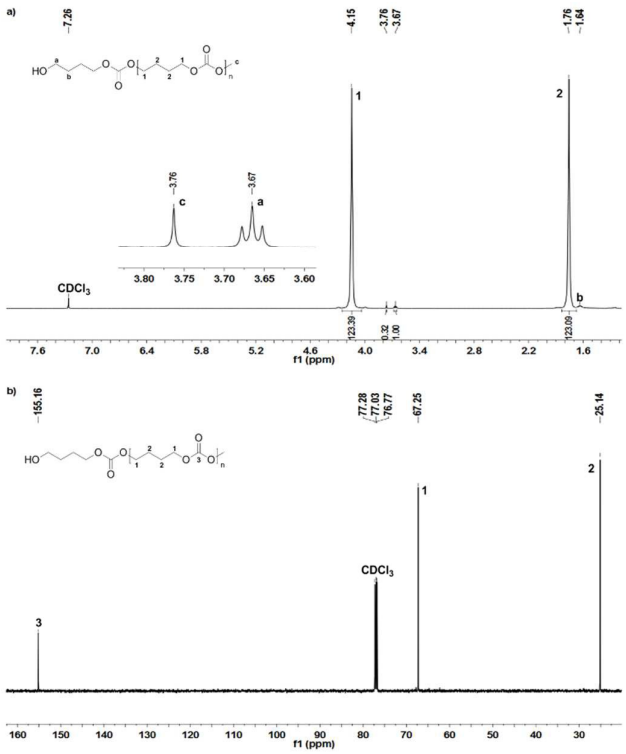


Figure 2. ^{1}H (a) and ^{13}C NMR (b) spectra of PBC 9

In addition, the end group ratio in the resulting polymers could be adjusted by changing the initial feed ratios, catalysts, or polymerization temperatures. The hydroxyl end group content decreases from 86 % to 20 % with increasing initial concentration of DMC (entry 2 and 3). When the polymerization was conducted using lower amount of catalyst, PBC with higher hydroxyl content (98 % -OH end group) was obtained. The end group composition can also be controlled by using various catalysts due to their different catalytic activities (entry 3 and 9). Using cat. 5 leads to a PBC with 20 % -OH end group, while a PBC with 68 % -OH end group could be prepared at the same feed ratio of [diol] : [DMC] : [cat.] = 1 : 2 : 0.01, when DMAP (cat. 1) was used. Besides, polymerization temperature is also an important factor in controlling the end group composition. The hydroxyl content decreased from 68 % to 30 % with the temperature increasing from 130 °C to 170 °C (entry 9 and 10). By studying the preparation of polycarbonate with defined end group composition, we found that hydroxyl terminated PBCs, which are of great interest, especially for further terminal group modification, could be obtained by using different catalysts (0.5 mol-%) with the initial feed ratio of [BD] : [DMC] < 1 : 1.2 (entry 4 - 8). Among them M_n determinated for the samples using DMAP and MTBD as catalysts (entry 4 and 6) were obtained up to 17000 g/mol and the dispersities were lower than 1.8. Polymers synthesized using PPY based catalysts (entry 5 and 7) showed lower M_n and higher $Đ_M$ ($Đ_M$ > 2) in contrast to DMAP and MTBD. The lower catalytic activity of PPY based catalysts in the 2. step is probably reflective of the decreased nucleophilic properties for the transesterification reaction between two methyl carbonate end groups. According to our research results, polycarbonates with

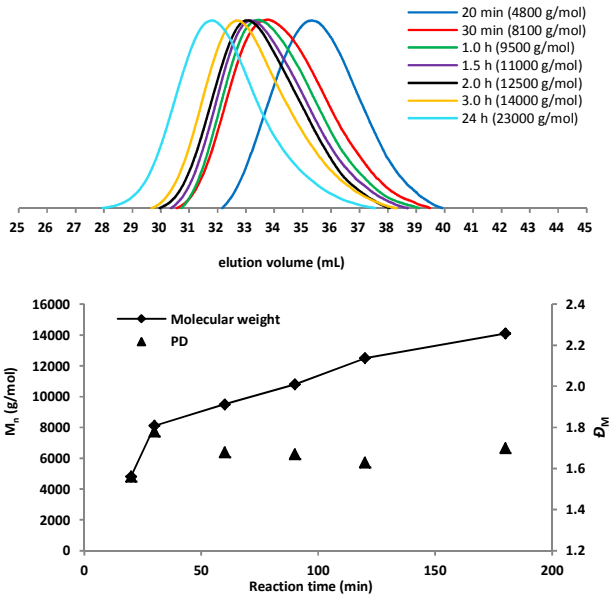


Figure 3. SEC traces and plot M_n (determined by SEC) and dispersity values of PBC 9 versus polymerization time in the 2. step.

defined M_n, end group composition and low dispersity could be achieved by using alterable initial feed ratios, polymerization temperatures and catalysts with different activities.

The ^{1}H and ^{13}C NMR spectra of PBC 9 are shown in Figure 2. Two multiplet signals at 1.76 ppm and 4.15 ppm are attributed to the both CH_2-group in the polymer backbone. The small signals at 1.64 ppm and 3.67 ppm indicated the existence of terminal butanol group, while the singlet at 3.76 ppm is assigned to the terminal methyl carbonate group. The ^{1}H NMR spectroscopy indicated that no decarboxylation occurred because no ether linkage (CH_2-O-CH_2) at 3.4 - 3.5 ppm was detected. In addition, comparing the peak areas of the terminal butanol and methyl carbonate group the hydroxyl content could be calculated. For the samples with pure hydroxyl end group only two signals at 1.64 ppm and 3.67 ppm were detected, while the singlet peak at 3.76 ppm for -C(O)OCH_3 was not visible. In the ^{13}C NMR spectrum, the peaks around 25.14 ppm and 67.25 ppm correspond to C1 and C2 carbon atoms of polymer backbone, respectively. The carbonate group is observed at 155.16 ppm. Signals of terminal groups are absent in ^{13}C NMR spectrum.

To determine the influence of polymerization times on the molar mass of PBC, a kinetic study of PBC 9 ([BD] : [DMC] : [DMAP] = 1 : 2 : 0.01, 130 °C) was carried out. Figure 3 shows molar mass and molar mass distribution data determined by SEC. The molar mass of the polymer increased rapidly throughout the initial 30 min. After a reaction time of 3 h, a molar mass of 14000 g/mol was obtained.

When the condensation reaction was further conducted the molar mass increased slower up to finally M_n = 23000 g/mol for 24 h reaction time. The dispersity values remained below 1.8 during the condensation reaction.

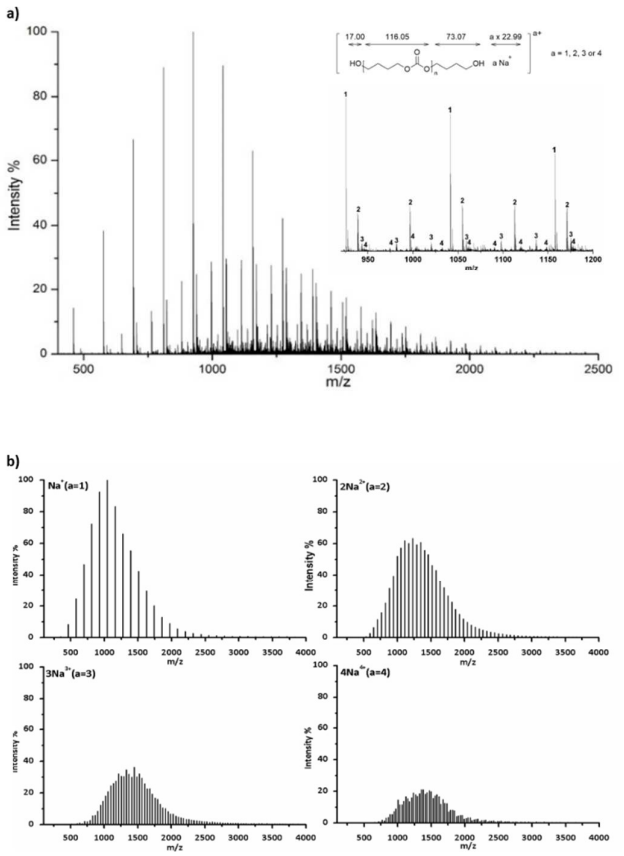


Figure 4. ESI-ToF mass spectrum of PBC 7 (Table 2, entry 7) terminated with hydroxyl group, a) complete spectrum and a part of the spectrum distinguished by carrying charges a = 1, 2, 3 and 4 in the region m/z 400 to 2500, and b) separated spectra with a = 1, 2, 3 and 4

Hydroxyl terminated PBCs (PBC 4 - 9 in Table 2) have also been investigated by ESI-ToF-MS to determine the end groups. Figure 4a shows a typical ESI-ToF-MS spectrum for hydroxyl terminated PBC. Polymers were multiply charged during the ionization. The different series can be separated by Ion Mobility Separation (IMS).[35] Separated spectra of up to tetraly charged polymers are shown in Figure 4b. Moreover, the pentaly and hexaly charged polymers were also detected but they are distributed with low intensity. ESI-ToF-MS spectra shows the presence of main series of polymer chains corresponding to $(HO\text{-}PBC\text{-}C_4H_8OH\ a{\cdot}Na)^{a+}$ (a = 1, 2, 3 or 4) with repeating units of 116.05 Da, which is the molar mass of repeating PBC unit. For the doubly charged polymer with n = 20 (Table 3, entry 2), the measured value of 1229.36 Da corresponded to the calculated value of 1229.19 Da using Eq. 2. No further series could be seen, indicating that the polymer was only terminated with hydroxyl groups at the both chain ends. Hence, the organo-catalyzed synthesis of polycarbonates proceed successfully without any side reaction, such as decarboxylation.

$$m/z = \frac{M(BD)+M(monomer\ unit)\times n+a\times Na^+}{a} \qquad \text{(Eq. 2)}$$

The thermal properties of PBC, PPC and PHC samples were evaluated by DSC as shown in Table 4. The PBC samples displayed glass transition temperatures (T_g) of -36 - -31°C and T_g increases with increasing molar mass. The T_g of PHC sample tended to lower T_g due

Table 3. Calculated and experimental m/z in ESI-TOF mass spectrum of PBC 7 with different charges (a up to 4)

a	Calculated [Da]	Found [Da]	Calculated [Da]	Found [Da]	Difference [Da]
1	1042.01	1042.19 (n=8)	1158.12	1158.33 (n=9)	116.14
2	1229.19	1229.36 (n=20)	1287.24	1287.37 (n=21)	58.01
3	1214.18	1214.38 (n=30)	1252.88	1253.06 (n=31)	38.68
4	1206.67	1206.86 (n=40)	1235.69	1235.91 (n=41)	29.05

Table 4. Thermal properties of aliphatic polycarbonate samples

	M_n[1] (g/mol)	T_g (°C)[2]	T_m (°C)[2]
PBC 5	7900	[3]	59.9
PBC 4	16000	-35.9	61.6
PBC 9	23000	-33.2	59.0
PBC 10	52000	-31.9	56.4
PPC 1	22000	-42.4	54.2
PHC 1	23000	-38.6	55.5

[1] determined using SEC in chloroform with PS standards
[2] T_g and T_m were measured by DSC
[3] Not detected

to the higher chain flexibility. The melting temperatures (T_m) were observed at 56 - 62°C, while the PPC and PHC showed lower T_m. In our case, the T_g were not visibly affected by the nature of chain end group compositions.

Conclusions

In summary we demonstrated that the commercially available organo-catalysts DMAP, PPY, TBD and MTBD were suitable for the synthesis of aliphatic polycarbonates with high molar mass and low dispersities via a two-step condensation polymerization under relatively mild operating conditions. Poly(1,4-butylene carbonate) (PBC), poly(1,5-pentamethylene carbonate) (PPC) and poly(1,6-hexametylene carbonate) (PHC), were successfully prepared with M_n up to 23000 g/mol, dispersities below 1.80 and yields of > 80 % at 130 °C using 4-dimethylaminopyrridine (DMAP) as catalyst. At 170 °C molar mass of poly(1,4-butylene carbonate) increased up to 52000g/mol.

In addition, according to our results polycarbonate with defined M_n, end group composition and low dispersity could be achieved by

changing initial feed ratios, polymerization temperatures and catalysts with different activities. Remarkably, depending on the initial feed ratio ([BD] : [DMC] < 1 : 1.2), hydroxyl terminated polycarbonates with different molar mass can also be obtained with high molar mass (up to 17000 g/mol, $Đ_M$ = 1.77). These materials are of great interest, because the combination with other polymerization method, such as controlled radical polymerization (ATRP, RAFT or NMRP) for further application and thermal properties improvement is allowed by end group modification. Additionally, the thiourea based organo-catalysts retarded the transesterification and condensation polymerization steps. On the other hand, that also proved why the thiourea based catalysts could be used in the ring opening polymerization of cyclic ester or carbonates and inhibits simultaneously the transesterification side reaction.

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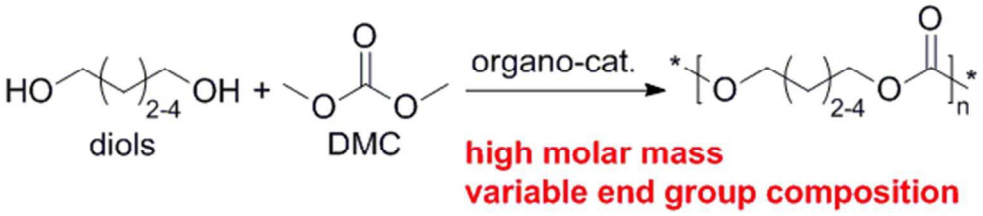

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