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NEW POLYMER SYNTHESES 106. POLYCARBONATES BY RING-OPENING POLYCONDENSATIONS OF TIN-CONTAINING MACROCYCLES WITH BISCHLOROFORMATES

Hans R. Kricheldorf[a]; Zaza Gomourashvili[a]; Dennis Langanke[a]
[a] Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

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NEW POLYMER SYNTHESES 106. POLYCARBONATES BY RING-OPENING POLYCONDENSATIONS OF TIN-CONTAINING MACROCYCLES WITH BISCHLOROFORMATES

Hans R. Kricheldorf,* Zaza Gomourashvili, and Dennis Langanke

Institut für Technische und Makromolekulare Chemie
Bundesstr. 45
D-20146 Hamburg, Germany

Key Words: Macrocycles, Bischloroformates, Polycarbonates, Ring-Opening Polycondensation, Tin Alkoxides

ABSTRACT

2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was polycondensed with bisphenol-A bischloroformate (BABC) in bulk. Regardless of the reaction temperature and time only number average molecular weights (M_ns) around 8,000-11,000 were obtained. ^{13}C NMR spectra proved that the isolated copoly-carbonates possessed a random sequence. MALDI-TOF spectra of the crude and of the fractionated samples revealed that all samples contained macrocyclic polycarbonates. DSDOP was also used as initiator for the macrocyclic polymerization of-cap-rolactone. The resulting cyclic polylactones were then polycon-densed with BABC *in situ*. M_ns in the range of 25,000-40,000 and M_ws in the range of 40,000–65,000 were found based on polystyrene calibrated GPC measurements. Similar results were obtained when 1,6-hexanediol bischloroformate was used as electrophilic reaction partner in the polycondensation step.

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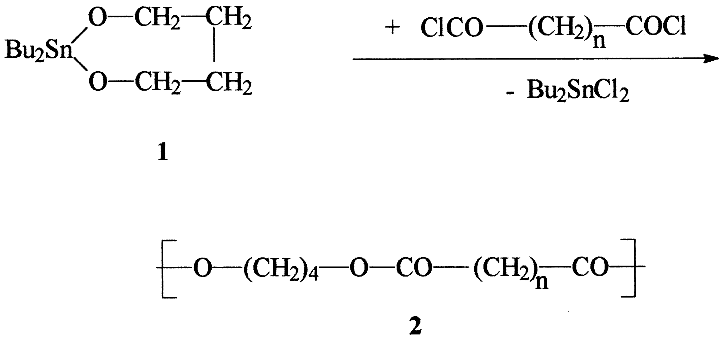
*Author to whom correspondence should be addressed.

INTRODUCTION

In previous publications in this series [1-3], we have presented a new synthetic strategy, namely, the ring-opening polycondensation of tin containing (macro)cycles. When the seven membered ring **1** (2,2-dibutyl-2-stanna-1,3-dioxepane, DSDOP) was mixed with dicarboxylic acid chlorides exothermic polycondensations took place (Equation 1) which yielded polyesters having M_ns of the order of 10,000-30,000 [2]. The reaction products **2** are of particular interest for two reasons. First, they are biodegradable semicrystalline engineering plastics, two of which have been commercialized (prepared by another procedure). Second, it was found by means of MALDI-TOF spectroscopy that those polyesters mainly consist of (super)macrocycles, although all polyconden-sations were conducted in bulk under conditions which exclude equilibration and back-biting degradation via transesterification.

Furthermore, DSDOP was used as an initiator for the macrocyclic polymerization of ε-caprolactone (ε-CL) and other lactones [1, 4] (Equation 2). These polymerizations exclusively yielded cyclic polymers (**3**, Equation 3), which were used *in situ* as bifunctional monomers or ring-opening polycondensations (Equation 3) [1]. Polylactones of structure **4** were obtained having M_ns up to 10^5 Da. Analogous combinations of ring-opening polymerization and polycondensation (ROPPOC method) were conducted with dicarboxylic acid bisthiophenyl esters [3]. In this connection the present work served two purposes. First, it should be found out, if tin-containing heterocycles such as **1** and **3** allow successful polycondensations with bischloroformates as electrophilic reaction partners. The results of these polycondensations were not predictable, because model reactions did not exist. Furthermore, the byproduct Bu_2SnCl_2 cannot be removed from the reaction mixture (because it is not crystalline and not volatile enough), so that the reaction enthalpies decide about the success of the polycondensations. The second purpose of this work was to elucidate, if the polycondensation products possess a linear or cyclic structure.



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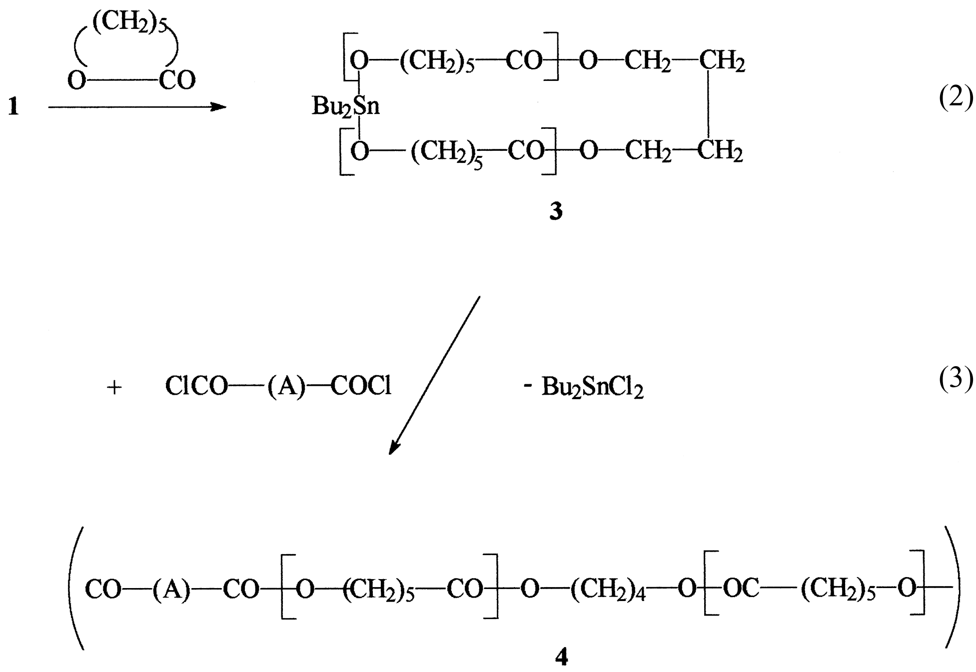
(1)

2



3

(2)

(3)

4

EXPERIMENTAL

Materials

1,4-Butane diol, 1,6-hexane diol, dibutyltin dichloride and ε-caprolactone (Equation ε-CL) were purchased from Aldrich Co. (Milwaukee, WI, USA). The ε-CL was distilled *in vacuo* over freshly powdered calcium hydride prior to its polymerization. The DSDOP was prepared from dry 1,4-butane diol and dibutyltin dimethoxide (obtained from dibutyltin dichloride and sodium methoxide in methanol) as described previously [1, 4]. The 1,6-hexane diol bischloroformate was prepared from 1,6-hexanediol and diphosgene according to the literature [5]. Bisphenol-A bischloroformate (BABC, m.p. 90-92°C) was a gift of Bayer AG, and was used as received.

Polycondensations of DSDOP (1)

Freshly distilled DSDOP (20 mmol) was weighed under dry nitrogen into a cylindrical glass reactor equipped with a mechanical stirrer, gas-inlet and gas-outlet tubes. The BABC (20 mmol) was added in the solid form (or as a 1 M solution in dry chlorobenzene). The reaction vessel was placed in an oil bath preheated to 80°C (in other experiments this temperature was raised to 120, 160, or 200°C within 20 minutes.). After 6 hours, the cold reaction product was dissolved in CH_2Cl_2 and precipitated into cold diethyl ether to avoid a methanolytic cleavage of carbonate groups.

Regardless of the reaction temperature (see Table 1), a random sequence was found by ^{13}C NMR spectroscopy and a glass-transition temperature (T_g) of 76-77°C by DSC.

Polycondensation of Free 1,4-Butane Diol

Bisphenol-A bischloroformate (15 mmol) was dissolved in dry CH_2Cl_2 (25 mL), dry 1,4-butane diol (15 mmol) was added, and finally a solution of pyridin (31 mmol in dry CH_2Cl_2 (10 mL)) was added dropwise with stirring. After 24 hours, the reaction mixture was twice extracted with water dried over Na_2SO_4 and precipitated into cold diethyl ether. After drying at 60°C *in vacuo:* yield 72%, $\eta_{inh} = 0.31$ dL/g in CH_2Cl_2, $T_g = 75°C$

ROPPOC Syntheses of Poly(ε-CL)

For the combined ring-opening polymerization and polycondensation (ROPPOC) of ε-CL the monomer (50 mmol) and a 1 M solution of DSDOP (2 mmol) in dry toluene were weighed into a cylindrical glass reactor equipped with a mechanical stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 65°C. After 1 hour, the BABC (2 mmol) or the hexane diol 1,6-bischloroformate (2 mmol) were added in the form of a 1 M solution in dry chlorobenzene. The temperature was raised to 80°C (or higher, see Tables 2 and 3) and the polycondensation was continued for 16 hours. Finally, the cold product was dissolved in CH_2Cl_2, precipitated into cold methanol and dried at 40°C *in vacuo*.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C.

The DSC measurements were conducted with a PERKIN ELMER DSC-7 in aluminum pans under nitrogen at a heating rate of 20°C/min.

The 25.2 MHz ^{13}C NMR spectra were recorded on a Bruker AC-100 FT NMR spectrometer in $CDCl_3$/TMS, using 10 mm o.d. sample tubes.

The GPC measurements were conducted with a Kontron HPLC apparatus equipped with a Waters differential refractometer Md 410. Four Ultra-styragel®

columns, having pore sizes of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} Å were used in combination with tetrahydrofuran as eluent.

The MALDI-TOF mass spectra were recorded with a Kratos Kompact MALDI III (Shimadzu) using a nitrogen laser source (λ = 337 nm), a positive polarity and 20 kV acceleration voltage in the reflextion mode. Tetrahydrofuran served as a solvent and 2, 4, 5-trihydroxyacetophenone as matrix. Bovine insulin was used for calibration.

RESULTS AND DISCUSSION

Polycondensations of DSDOP

A first series of ring-opening polycondensations was conducted in such a way that DSDOP (**1**) was reacted with BABC under conditions which allowed a direct comparison with our previous polycondensations based on dicarboxylic acid dichlorides (Equation 1). The reaction conditions and results were summarized in Table 1. Polycondensations occured in all experiments and the viscosity or molecular weight measurements revealed a couple of interesting tendencies.

TABLE 1. Ring-Opening Polycondensations of DSDOP (1) with Bisphenol-A Bischloroformate

Polym. No.	Temp. (°C)	Time (h)	Yield (%)	η_{inh} [a] (dL/g)
1[b]	80	6	41	0,22
2	80	6	64	0,29
3	80	24	67	0,31
4	120	6	72	0,32
5	160	6	77	0,33[c]
6	200	6	77	0,30

a) measured at 20°C with c = 2 g/L in CH_2Cl_2

b) the BABC was added in the form of a 1 M solution in chlorobenzene

c) GPC measurements calibrated with polystyrene gave: M_n = 11 000 and M_w = 17 000

First, the addition of BABC in the form of a 1 M solution was inferior to an addition of solid BABC. Second, the molecular weights were rather low in all cases. Polystyrene calibrated GPC measurements suggested number average molecular weights (M_ns) of 8,000-11,000 and weight average molecular weights (M_ws) in the range of 13,000–17,000 (for samples No. 2-6, Table 1). Third, the variation of reaction time and temperature had little influence on both yields and molecular. The observation that even at 200°C, no significant degradation took place is remarkable is. A similar result was reported for the polycondensations of Equation 1.

It seems as if the chain growth is systematically hindered by an unfavorable equilibrium or by a side reaction concerning the functional groups.

However, polycondensation at 80°C represent rather mild conditions which should not affect the stability of the chloroformate groups. This conclusion is supported by the result of the polycondensations performed at 120 and 160°C.

The structure of the polycarbonates **5** was characterized by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra showed the expected signals of the butylene unit and of the bisphenol-A moiety with an intensity ratio of 1:1 according to structure **5.** More informative were the ^{13}C NMR spectra which displayed three sharp CO-signal as illustrated in Figure 1. When ^{13}C NMR spectra of poly (bisphenol-A carbonate) and poly(trimethylene carbonate) were recorded under the same conditions, CO-signals at 152.1 and 154.9 ppm were found. These different chemical shifts proved that the polycarbonates prepared from DSDOP possess a perfectly random sequence when prepared at 200°C and even at 80°C a nearly random sequence was obtained (Figure 1).

In order to find out if the equilibration reactions takes place in the first stage of the polymerization process between the functional groups, or in a later stage by ester-ester interchange the following model reaction was conducted. An equimolar mixture of poly(bisphenol-A carbonate) and poly(trimethylene carbonate) was heated to 80°C in concentrated 1,2-dichloroethane solution and a stoichiometric amount of Bu_2SnCl_2 was added according to the conditions of the polycondensation (Equation 4). The polymers isolated after 6 hours at 80°C turned out to be a mixture of two homopolycarbonates without any indication of trans-esterification (two CO-signals at 154.9 and 152.1 ppm were observed). This result suggests that the equilibration takes place via the functional groups either catalyzed by Bu_2SnCl_2 (Equations 5-8) or catalyzed by the Sn-O bonds of DSDOP.

A further model reaction was performed by polycondensation of 1,4-butandiol and BABC with addition of pyridin as HCl acceptor and catalyst (eq. (9)). From this experiment a polycarbonate having an alternating sequence was isolated as indicated by the ^{13}C NMR-spectrum which only exhibited one sharp

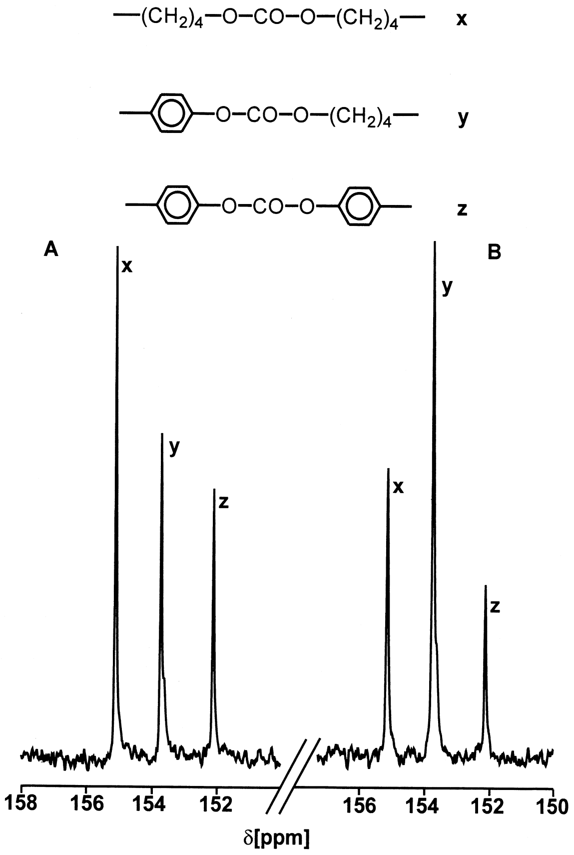
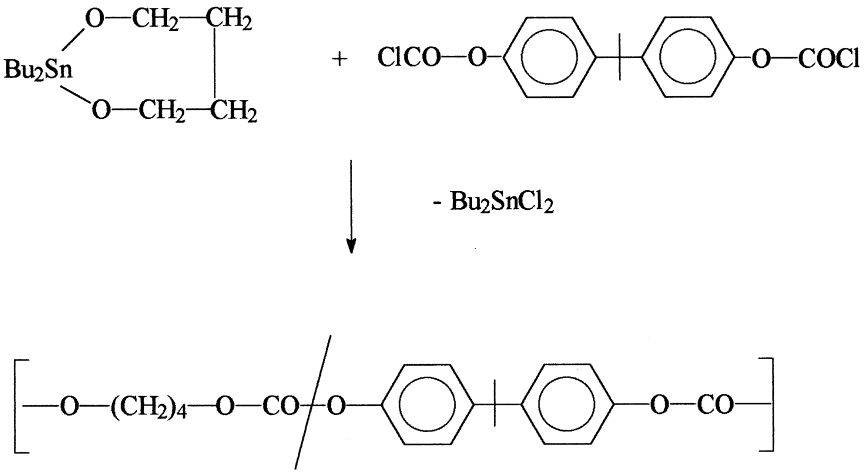


Figure 1. ^{13}C NMR spectra (CO-signals only) of: A) polycarbonate **5** (No. 2, Table 1), B) polycarbonate **5** (No. 6, Table 1).

CO-signal at 153.7 ppm. This result definitely proves the correct interpretation of all ^{13}C NMR spectra.

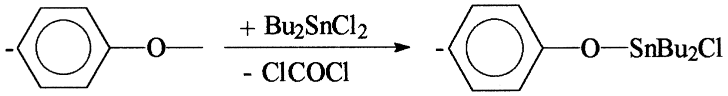
In this connection, a characterization of the random copolycarbonates **5** by MALDI-TOF mass sspectrometry was of interest. Three samples (Nos. 2, 4, and 6 of Table 1) were analyzed, and in all three cases cyclic oligocarbonates having an equimolar composition of butane-diol and bisphenol-A were detected among the reaction products. A further series of signals were assigned to linear oligomers (and polymers) having the structure **7** or **8**. A complete assignment of all mass peaks was not achieved, because not all oligo-(polycarbonates) possessed an equimolar composition of 1,4-butane diol and bisphenol-A unites.

Finally, the thermodynamical aspect of this ring-opening polycondensation needs a short discussion. Since the byproduct Bu_2SnCl_2 cannot only be

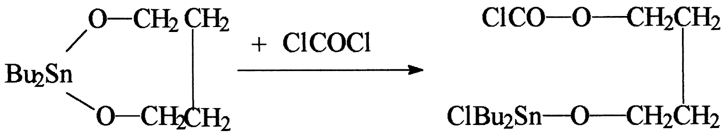


(4)

5 (random sequence)



(5)



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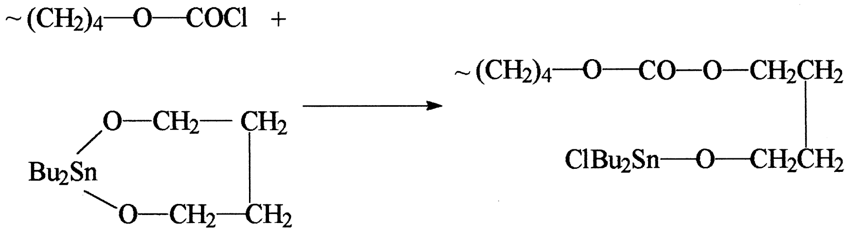

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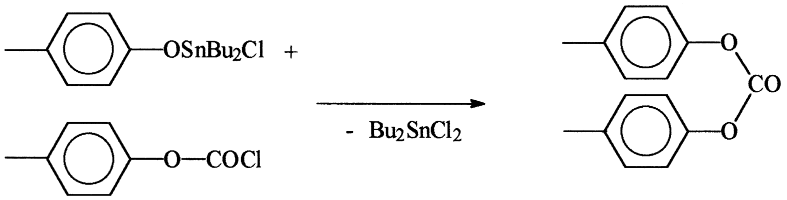

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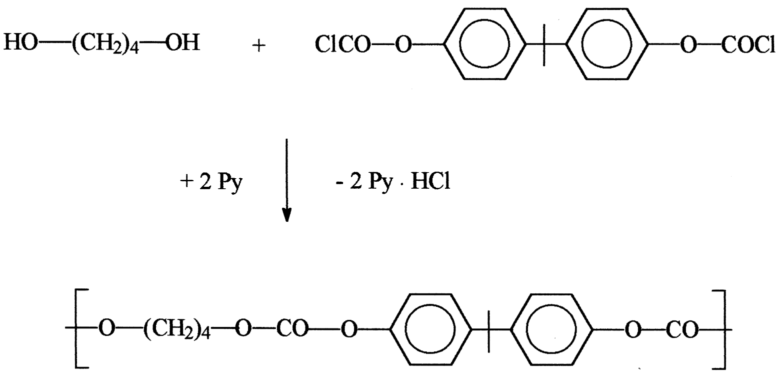
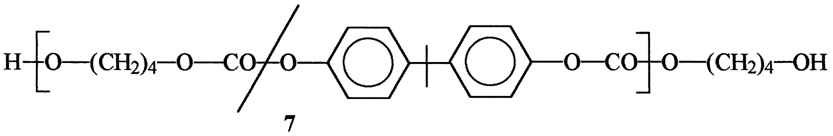


(9)

6 (alternating sequence)



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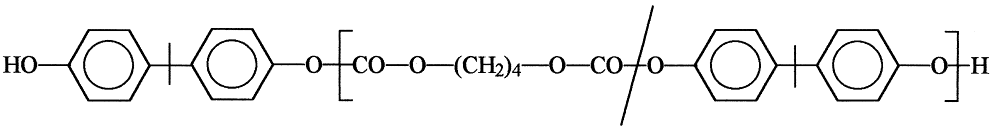


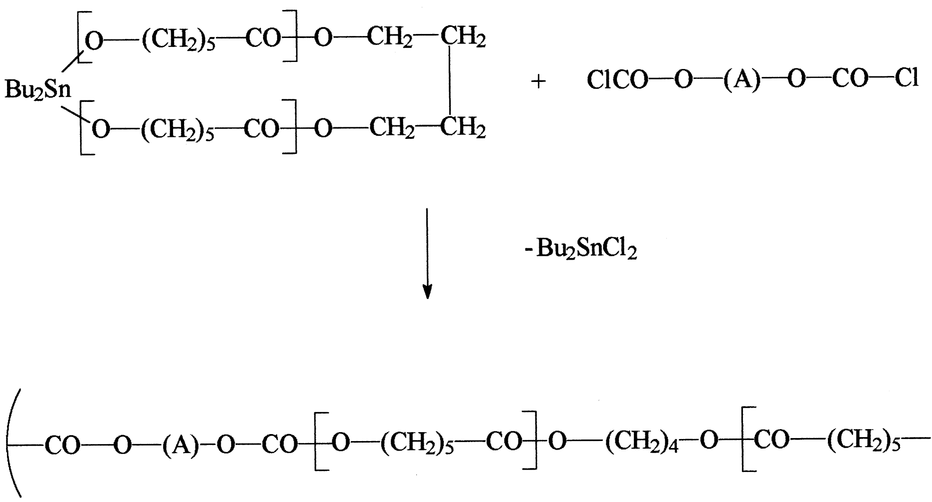
8

removed from the reaction mixture, this polycondensation ends up in an equilibrium which depends on the reaction enthalpy. Therefore, it was of interest to get at least a crude idea how the exothermic character of polycondensations involving bischloroformates compares to that of polycondensations involving dicarboxylic acid dichlorides (Equation 1). For this purpose, concentrated solutions of BABC or of 1,10-decane dicarbonylchloride in chlorobenzene were reacted with DSDOP at 20°C. These reaction mixtures possessed nearly identical heat capacities, and thus, a crude comparison was feasible by measurements of the reaction temperature. An increase of 82°C was found for BABC and an incrase of 85°C for the decane 1,10-dicarbonyl dichloride. Therefore, it may be concluded that the reaction enthalpy of the DSDOP/BABC system is quite similar to that of DSDOP/aliphatic dicarboxylic acid chlorides. Obviously, the lower molecular weights obtained for the polycarbonates **5** are a consequence of more side reaction and incomplete conversion and not a consequence of a thermodynamically less favorable polycondensation equilibrium.

Polycondensation of Cyclic poly (ε-CL)

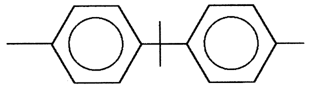
Macrocyclic poly (ε-CL) was prepared by DSDOP initiated polymerization of ε-CL in bulk. As reported previously [4], the use of the seven membered DSDOP as initiator enables a control of the molecular weight via the monomer/initiator (M/I) ratio in contrast to five or six-membered cyclic tin alkoxides [5, 6]. In this work, the polymerizations of ε-CL were conducted with M/I ratios of 25/1, 50/1, and 100/1 to obtain cyclic polylactones of different ring size and molecular weight. These macrocycles were polycondensed with BABC *in situ* (Equation 9)). As demonstrated by the results compiled in Table 2, the molecular weights of the isolated polylactones of structure **9a** reflect the different molecular weights of the macrocycles used as monomers. The same trend was observed for polycondensations of tin-containing poly (ε-CL) with terephthaloyl chloride or sebacoyl chloride (Equations 2 and 3) [1]. When the macrocyclic poly (ε-CL) of DP (degree of polymerization) 50 was polycondensed at three different temperatures, almost identical results were obtained. In this respect, a close analogy to the polycondensations of DSDOP itself (Table 1) became evident.

A further series of ring-opening polycondensations of macrocyclic poly (ε-CL) was conducted with 1,6-hexamediol bischloroformate as reaction partner, so that polyesters of structure **9b** were obtained. The molecular weights of these polylactones (listed in Table 3) again reflect the ring size of the macrocyclic monomers (i.e., the M/I ratios) and again, the variation of the temperature had no influence on the molecular weights. These trends agree perfectly with those



(10)

9a, b

a : A = 

b : A = $—(CH_2)_6—$

observed for the poly condensations of BABC, and indicate a good reproducibility of the main effects influencing these polycondensations.

The molecular weights of the polylactones **9a** and **9b** were characterized by GPC measurements in tetrahydrofurane. The election curves were evaluated in two ways. Either the K and a values published for polystyrene in tetrahydrofuran solution (Equation 11)) were used [7], because calibration with polystyrene is the most widely used procedure for the evaluation of GPC measurements. However, it was shown in a previous publication [4] that polystyrene based GPC calibration overestimates the real molecular weights of poly(ε-caprolactone). Therefore, the alternative calibration with the M.-H-equation (12) relaborated by Schindler *et al.* [8] for solutions of poly(ε-caprolactone) in THF was also used (Tables 2 and 3). The lower values obtained in this way may be considered to match the real molecular weights. Yet, also these lower molecular weights demonstrate that the polycondensation steps have brought about a moderate chain extension. A rather low chain extension factor for Sn-containing polylactones and high chain extension factor for DSDOP were also observed for ring-opening poly-condensations

TABLE 2. Polycondensations of macrocyclic Poly(ε-CL) with Bisphenol-A Bischloroformate

Polym. No.	Ring-opening polymerization			Reaction conditions and results of the ring-opening polycondensation							
	$\frac{Mon^{a)}}{Init}$	$\eta_{inh.}$ b) (dL/g)	M_n c) calcd.	Temp. (°C)	Time (h)	Yield (%)	η_{inh} b) (dL/g)	M_n c) (GPC)	$\frac{M_w}{M_n}$ c)	M_w d) (GPC)	$\frac{M_w}{M_n}$ d)
1	25/1	19	2 800	80	16	84	0.38	16 000	1.45	24 000	1.50
2	50/1	31	5 700	80	16	88	0.42	17 000	1.45	28 000	1.50
3	50/1	31	5 700	130	16	96	0.41	17 000	1.45	27 000	1.50
4	50/1	31	5 700	180	24	94	0.42	20 000	1.50	32 000	1.55
5	100/1	47	11 500	80	16	95	0.58	29 000	1.60	47 000	1.70

a) ε-CL/DSDOP of the ring-opening polymerization performed in bulk at 65°C/1h

b) measured at 20°C with c = 2g/L

c) GPC measurements in THF calibrated with the M.H. equation (12)

d) GPC measurements in THF calibrated with eq. (11)

TABLE 3. Ring-Opening Polycondensations of Macrocyclic Poly(ε-CL) with 1,6-Hexanediol Bischloroformates

Polym.	Ring-opening polymerization			Reaction conditions and results of the ring-opening polycondensations							
No.	$\frac{Mon^{a)}}{Init}$	$\eta_{inh.}$ (dL/g)	M_n calcd.	Temp. (°C)	Time (h)	Yield (%)	η_{inh}[b)] (dL/g)	M_n[c)] (GPC)	$\frac{M_w}{M_n}$[c)]	M_n[d)] (GPC)	$\frac{M_w}{M_n}$[d)]
1	25/1	19	2 800	80	16	84	0.51	15 000	1.50	24 000	1.55
2	50/1	31	5 700	80	16	96	0.62	20 000	1.45	31 000	1.50
3	50/1	31	5 700	80	32	96	0.61	19 000	1.45	30 000	1.50
4	50/1	31	5 700	130	16	95	0.60	19 000	1.45	30 000	1.50
5	100/1	47	11 500	80	16	97	0.65	21 000	1.45	32 000	1.50

a) ε-CL/DSDOP ratio of the ring-opening polymerizations performed in bulk at 65°C/1h

b) measured at 20°C with c = 2g/L in CH_2CL_2

c) GPC measurements in THF calibrated with the M.H. equation (12)

d) GPC measurements calibrated with eq. (11)

with aliphatic dicarboxylic acid dichlorides. The reason for this difference is not clear at this time, but it is currently under investigation.

$$[\eta] = 1.25 \times 10^{-4} \times M_w^{0.717} \tag{11}$$

$$[\eta] = 1.395 \times 10^{-4} \times M_w^{0.786} \tag{12}$$

CONCLUSION

The results of the present study indicate that the concept of "ring-opening polycondensation" may successfully be applied to combinations of cyclic tin alkoxides and aliphatic or aromatic bischloroformates. When small tin cycles are used as monomers, such as DSDOP, M_{ns} up to 10,000 Da can be obtained. The chain growth seems to be limited by cyclization reactions. The tin alkoxide groups also cause transesterification, and thus, the formation of copolycarbonates having random sequences. Ring-expansion polymerization of lactones and chain extension with bischloroformates can be combined in an one-pot reaction.

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