Competing Cyclization and Chain Growth in *tert*-Amine-Catalyzed Polycondensations of Bisphenol A with Bisphenol A Bischloroformate

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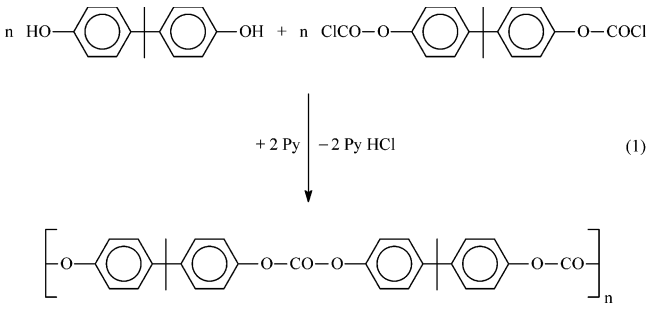
ABSTRACT: Bisphenol A was polycondensed with bisphenol A bischloroformate (BABC) in CH_2Cl_2 at 5, 20, and 40 °C using pyridine as catalyst and HCl-acceptor. The feed ratio was varied, and the maximum molecular weight was obtained with a 10 mol % excess of BABC. The MALDI−TOF mass spectra exclusively displayed peaks of cycles. Because of disproportionation of chloroformate groups, small amounts of odd-numbered cyclocarbonates were formed in addition to the prevalent even-numbered ones. Triethylamine as catalyst gave lower molecular weights, a maximum at 4 mol % excess of BABC and only traces of odd-numbered cycles. With *N*-ethyl diisopropylamine again, traces of odd-numbered cycles and the lowest molecular weights were obtained due to intensive side reactions. Model reactions with phenyl chloroformate and BABC indicated that pyridine catalyzes a disproportionation of chloroformate groups yielding carbonate groups in the absence of phenols or water. These polycondensations in a homogeneous organic phase yielded cyclic polycarbonates of much lower molecular weight than interfacial hydrolytic polycondensations of BABC. This finding indicates that, in contrast to comments in the literature, the interfacial polycondensations are less favorable for cyclization reactions.

Introduction

The pyridine-catalyzed polycondensation of diphenols with their bischloroformates in dichloromethane was the first method designed for the synthesis of cyclic oligo- and polycarbonates, and cyclic tetramers of several diphenols were prepared in this way[1,2] (eq 1). Later repetitions of such syntheses with bisphenol



(1)

A and BABC by Brunelle et al.[3] and by Kricheldorf et al.[4] revealed that in addition to the expected even-numbered cyclocarbonates, small amounts of odd-numbered cycles were formed. However, a detailed study of these polycondensations has never been published to the best of our knowledge. Another approach yielding cyclic oligo- and polycarbonates is the "hydrolytic polycondensation" of BABC. This approach first reported by Horbach et al.[5,6] was later optimized by Brunelle et al. for the preparation of cyclic oligocarbonates by means of the pseudo-high dilution method (Rüggli-Ziegler dilution principle).[3,7−9] High molar mass polycarbonates containing high molar mass cyclocarbonates were obtained by Kricheldorf et al.[10−12] when the hydrolytic polycondensation of BABC was performed in concentrated solution.

The present work had the purpose to study the polycondensation of BABC and bisphenol A in waterfree organic solvents in more detail. The influence of the reaction conditions on the competition between cyclization and chain growth should be elucidated. In kinetically controlled polycondensations such as the polymerization of bisphenol A with phosgene or BABC, cyclization competes with chain growth at any concentration and at any stage of the polycondensation.[4] Under optimum reaction conditions, the maximum molecular weight is limited by the efficiency of cyclization as formulated in eq 2.

$$\overline{DP} = \frac{1}{1 - p(1 - x^a)} \tag{2}$$

p = conversion

$a = V_{pr}/V_{cy}$ (rates of propagation vs cyclization)

x = factor (>1.0) allowing for an adaptaion to different concentrations

Therefore, the maximum molecular weight obtained under optimum conditions reflects the cyclization tendency of the system. Surprisingly, it was found that the optimized polycondensation of bisphenol A with di- or triphosgene in a waterfree organic phase[13] yielded significantly lower molecular weights than analogous interfacial polycondensations.[14,15] In other words, the interfacial polycondensations somehow suppress cyclization reactions in favor of the chain growth. In this context, the present work had the purpose to elucidate if the relationship between reaction conditions and cyclization tendency found for the "phosgenation" of bisphenol A is also valid for polycondensations of BABC. This study also required to find out how structure and reactivity of the *tert*-amine catalyst influence the results. Therefore, three different *tert*-amines (also used in interfacial polycondensations) were compared: pyridine, triethylamine, and *N*-ethyl diisopropylamine.

Experimental Section

Materials. Bisphenol A, phenyl chloroformate and bisphenol A bischloroformate (BABC) (purity > 99%) were kindly supplied by Bayer AG (Uerdingen, Germany) and bisphenol A was dried in vacuo over P_4O_{10} before use. Pyridine, triethylamine, and ethyl diisopropylamine (EDPA) were purchased from Aldrich Co. (Milwaukee, WI) and distilled over freshly powdered CaH_2. Sebacoyl chloride was also purchased from Aldrich Co. and distilled in vacuo prior to use.

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Table 1. Polycondensations of Bisphenol A and BABC Promoted with Pyridine

expt no.	excess of BABC (mol %)	temp (°C)	yield (%)	η_{inh}[a] (dL/g)	reaction products[b] (MALDI−TOF)
1	2	20	89	0.18	***C*** **+ La**
2	4	20	98	0.20	***C*** **+ La**
3	7	20	96	0.48	***C*** **+ (La)**
4A	10	20	98	0.56	***C***
4B	10	5	97	0.48	***C***
4C	10	40	95	0.36	***C***
5	15	20	97	0.53	***C***
6	20	20	99	0.18	***C*** **+ Ld + Le**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] The main products (below 5000 Da) are italicized.

Table 2. Polycondensations of Bisphenol A and BABC Promoted with Triethylamine at 20 °C

expt no.	excess of BABC (mol %)	yield (%)	η_{inh}[a] (dL/g)	reaction products[b] (MALDI−TOF)
1	0	92	0.25	***C*****, Ld, Lg, Le, Lh**
2	2	93	0.27	***C*****, Ld, Lg, Le, Lh, Lk**
3	4	99	0.30	***C*****, Ld, Lg, Le, Lh, Lk**
4	7	99	0.21	***C*****, Ld, Lg, Le, Lh, Lk**
5	10	99	0.13	***C, Ld*****, Lg, Le, Lh, Lk**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] The main products (below 5000 Da) are italicized.

Table 3. Polycondensations of Bisphenol A with BABC and Ethyl Diisopropylamine at 20 °C

expt no.	excess of BABC (mol %)	yield (%)	η_{inh}[a] (dL/g)	reaction products[b] (MALDI−TOF)
1	4	98	0.16	***C*****, Ld, Ll, Lm, Ln, Lo, Lp**
2	7	98	0.16	***C*****, Ld, Ll, Lm, *Ln*, Lo, Lp**
3	10	98	0.15	***C*****, Ld, Ll, Lm, *Ln*, Lo, Lp**
4	15	97	0.15	**C, Ld, Ll, Lm, *Ln*, Lo, Lp**
5	20	99	0.13	**C, Ld, Ll, Lm, *Ln*, Lo, Lp**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] The main products (below 5000 Da) are italicized.

Polycondensations. A. With Pyridine as Catalyst (Table 1). Bisphenol A (10.0 mmol, dried over P_4O_{10} in vacuo at 20 °C) and BABC (10.0 mmol) were dissolved in dry dichloromethane (180 mL), and a solution of dry pyridine (40 mmol) in dichloromethane (10 mL) was added dropwise with stirring. The reaction vessel was closed with glass stopper and stored at 20−22 °C. After 7 d, the reaction mixture was concentrated in vacuo (to a volume of approximately 50 mL) and poured into methanol (500 mL). The precipitated polycarbonate was isolated by filtration and dried at 60 °C in vacuo.

The polycondensation No. 4A was repeated with a bisphenol A dried over P_4O_{10} at 65 °C in vacuo. In a second repetition, pyridine was twice distilled over freshly powdered CaH_2 and the dichloromethane was twice distilled over P_4O_{10}, but the results (yields, viscosities, MALDI−TOF MS) of all these repetitions were nearly identical.

The polycondensation 4B was conducted under cooling with an ice/salt mixture and the reaction mixture was stored in a refrigerator for 7 d. In the case of 4C (Table 1) the reaction time was shortened to 3 d.

B. With Triethylamine as Catalyst (Table 2). Dry bisphenol A (10.0 mmol) and BABC (10.0 mmol) were dissolved in dry dichloromethane (180 mL) and a freshly prepared solution of triethylamine (25 mmol) in dichloromethane (15 mL) was added dropwise with stirring. After 7 d, the reaction mixture was concentrated and precipitated into methanol containing 2 mL of formic acid.

C. With Ethyl Diisopropylamine (Table 3). Dry bisphenol A (10.0 mmol) and BABC (10.0 mmol) were dissolved in dry dichloromethane (180 mL), and a freshly prepared solution of EDPA (25 mmol) in dichloromethane (15 mL) was added dropwise with stirring. The reaction mixture was worked up as described for B).

Table 4. Polycondensations of Bisphenol A with Sebacoyl Chloride and Pyridine at 20 °C

expt no.	excess of sebacoyl chloride (mol %)	yield (%)	η_{inh}[a] (dL/g)
1	0	76	0.20
2	+1	81	0.22
3	+2	82	0.27
4	+4	88	0.25
5	+7	84	0.20
6	+10	76	0.17

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

D. With Sebacoyl Chloride and Pyridine (Table 4). Dry bisphenol A (10.0 mmol) and sebacoyl chloride (10.0 mmol) were dissolved in dry dichloromethane (180 mL), and a solution of dry pyridine (40 mmol) in dichloromethane (15 mL) was added dropwise with stirring. After 7 d at 20 °C, the reaction mixture was concentrated and precipitated into methanol.

Model Experiments. A. With Phenylchloroformate. Freshly distilled phenylchloroformate (20 mmol) and pyridine (20 mmol) were refluxed in dichloromethane (40 mL) for 48 h, from which a white product crystallized. After cooling to + 5 °C overnight the product was isolated by filtration and identified as diphenyl carbonate (yield 63%) by comparison of IR and ^{13}C NMR spectra with those of a commercial products.

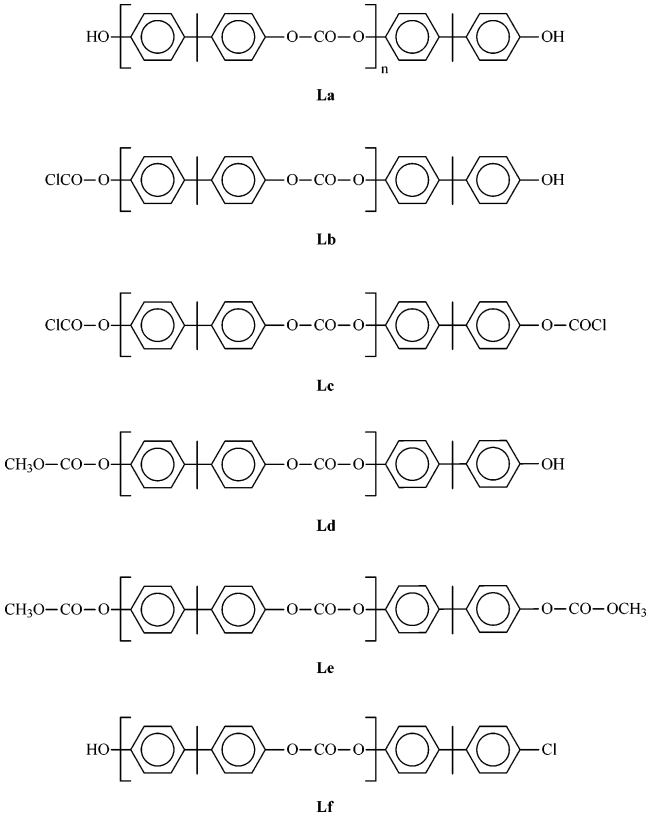
B. With BABC. BABC (20 mmol) and pyridine (80 mmol) were refluxed in CH_2Cl_2 (100 mL) for 24 h, whereby crystalline oligo carbonates precipitated from the reaction mixture. After the reaction mixture was cooled to + 5 °C overnight, the precipitate was filtered off, stirred with warm methanol for 30 min, and filtered again. An oligocarbonate was isolated in a yield of 42% having an inherent viscosity of 0.19 dL/g in CH_2Cl_2. The structure was identified by ^{13}C NMR and MALDI−TOF mass spectrometry.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MHz ^1H NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference. The MALDI−TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from $CHCl_3$ solutions using dithranol as matrix and K−trifluoroacetate as dopant.

Results and Discussion

Pyridine-Promoted Polycondensations. In the first publication describing the preparation of cyclic oligomers[1] of bisphenol A, pyridine was used as the catalyst. Therefore, the first series of polycondensations studied in this work was performed with pyridine as the catalyst and H−Cl acceptor. The reaction medium mainly consisted of dichloromethane for comparison with the previously studied interfacial polycondensations. However, dioxane was added for complete dissolution of bisphenol A. Furthermore, the concentration of the reactants was selected so that the final concentration of bisphenol A repeat units matched the concentration obtained in the interfacial polycondensations (0.1 mol/L). The results of these polycondensations are summarized in Table 1. They demonstrate that by variation of the stoichiometry the viscosity values passed a flat maximum around 10 mol % excess of BABC. A maximum of the molecular weight was also observed at an excess of 10 mol % of phosgene, when bisphenol A was polycondensed with diphosgene under the same reaction conditions and the inherent viscosity (0.52 dL/g) was nearly the same as those found in the present work (nos. 3−5, Table 1).

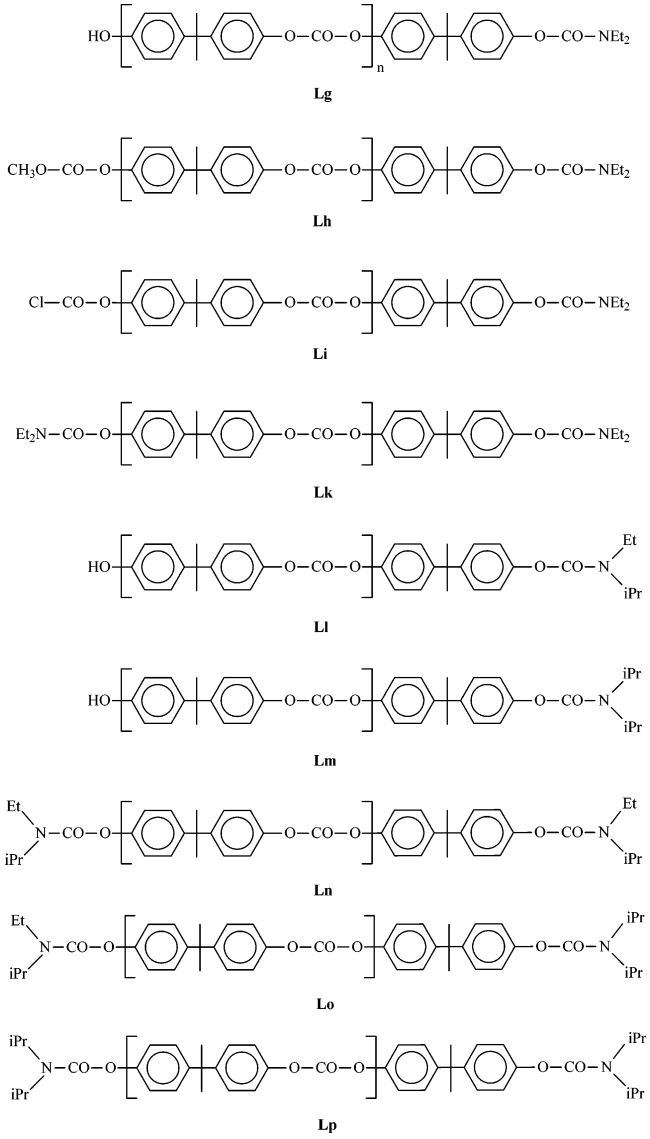
Scheme 1. Potential Reaction Products of Pyridine-Promoted Polycondensations



The MALDI−TOF MS revealed that those samples prepared with less than 10 mol % excess of BABC (nos. 1−3, Table 1) contained linear chains having two OH-end groups (**La** in Scheme 1) in addition to the cyclic polycarbonates. The molar fraction of the **La** chains decreased with increasing excess of BABC, and those samples prepared with 10 or 15 mol % excess exclusively displayed mass peaks of cycles as illustrated for no. 4A in Figure 1. With a larger excess of BABC (no. 6, Table 1) peaks of linear chains having one or two methyl carbonate end groups (**Ld** and **Le**, Scheme 1) became detectable. These end groups result from the precipitation of chloroformate-terminated polycarbonate chains (**Lb** and **Lc**) into methanol. This interpretation of the MALDI−TOF mass spectra was confirmed by ^{1}H NMR spectra. Sample nos. 1−3 displayed the typical doublet signals of protons neighboring the OH end group at 6.72 ppm. The ^{1}H NMR spectrum of sample no. 6, Table 1, exhibited a singlet signal at 3.91 ppm representing methyl carbonate end groups (all chemical shifts measured in $CDCl_3$/TMS).

An interesting feature of the MALDI−TOF MS was the presence of weak mass peaks resulting from odd-numbered cyclocarbonates. Together with the excess of BABC needed for maximum molecular weights, they indicate that the entire polycondensation process was more complex than outlined in eq 1. At this point, it should be emphasized that unusual end groups such as the chlorophenyl group in **Lf** were neither detected by mass spectroscopy nor by NMR spectroscopy. The formation of a chlorophenyl group by decarboxylation is unlikely under mild conditions, but pyridine catalyzes the formation of alkyl chloride groups by decarboxylation of aliphatic chloroformates. At first glance, it was suspected that small amounts of water caused hydrolysis of chloroformate groups. However, when the polycondensation was repeated twice using more intensively dried reagents, the results were

Scheme 2. Potential Reaction Products of Triethylamine- or Ethyl Diisopropylamine Promoted Polycondensations



the same. The odd-numbered cyclocarbonates had not vanished. Furthermore, the polycondensations of bisphenol A with sebacoyl chloride described below showed that if traces of water were present, they might be responsible for a consumption of 1−2 mol % excess of BABC but not for more. Moreover, in a reinvestigation of such polycondensations, Brunelle et al.[3] also detected the formation of small amounts of odd-numbered cyclopolycarbonates by means of HPLC.

Finally, two polycondensations were conducted with 10 mol % excess of BABC at a temperature of 5 and 40 °C respectively (nos. 4B and 4C, Table 1). Exclusively mass peaks of odd- and even-numbered cyclocarbonates were detected in the mass spectra and the molar fraction of odd-numbered cycles had slightly increased at the higher reaction temperature.

Triethylamine Promoted Polycondensations. Polycondensations of bisphenol A with BABC were conducted with triethylamine as catalyst and HCl-acceptor under the same conditions as the aforementioned pyridine-promoted polycondensations. However, the reaction products contained more methyl carbonate end groups (e.g., **Ld** chains) than expected. This finding suggested that a triethylamine-catalyzed methanolytic cleavage of cyclocarbonates took place during the precipitation and drying process. Therefore, the polycondensa-

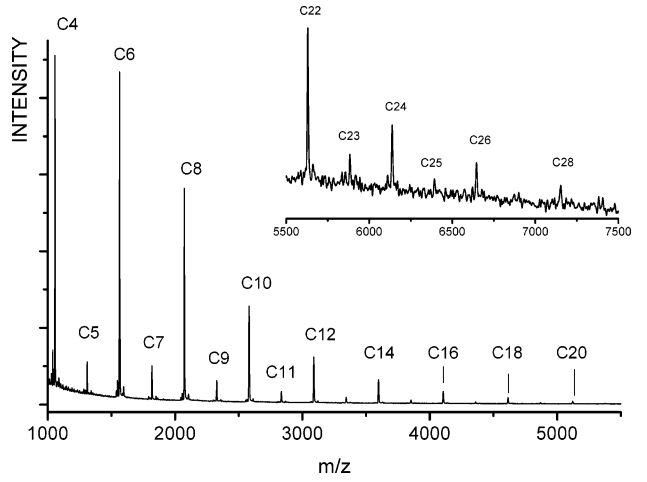


Figure 1. MALDI−TOF MS of the polycarbonate prepared with pyridine and 10 mol % excess of BABC at 20 °C (no. 4A, Table 1).

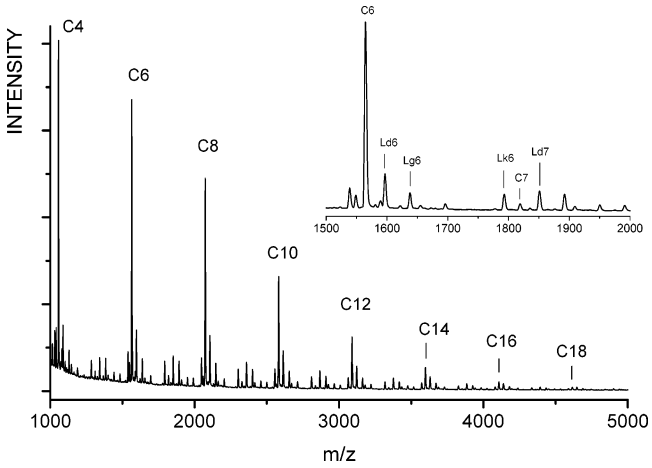
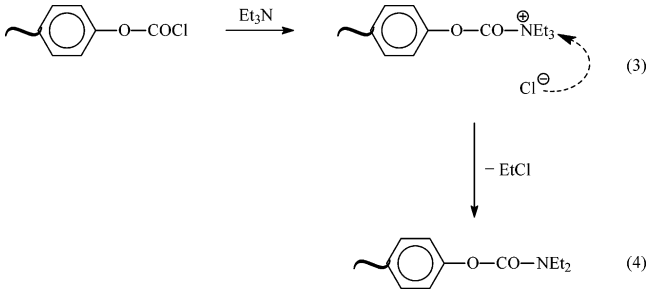


Figure 2. MALDI−TOF MS of the polycarbonate prepared with triethylamine and 4 mol % excess of BABC at 20 °C (no. 3, Table 2).

tions were repeated and formic acid was added to the methanol prior to the precipitation of the reaction mixture. The polycondensations performed in this way were compiled in Table 2. Characteristic for these results are molecular weights lower than those obtained with pyridine and a maximum between 4 and 7 mol % excess of BABC.

The MALDI−TOF spectra demonstrated that all polycarbonates contained large fractions of cycles. As illustrated by Figure 2, the cyclic polycarbonates were the largely prevalent products below 5000 Da under the optimum reaction conditions (no. 3, Table 2). Traces of the odd-numbered cycles **C3**, **C5**, and **C7** were also detected. Furthermore, small amounts of **Ld** chains having one methyl carbonate end group were found in all samples. Few **Ld** chains might have resulted from methanolytic cleavage of cyclic polycarbonates upon drying of the precipitated products. Yet, the main part has certainly resulted from reactions of chloroformate groups (**Lb** chains) upon precipitation into methanol. For the formation of the few **Le** chains, reaction of the bischloroformates (**Lc**) with methanol is the only plausible explanation anyway.

Characteristic for the use of triethylamine is the formation of diethylcarbamate end groups (**Lg**, **Lh**, and **Lk** chains). The **Lh** chains were most likely the consequence of reactions between methanol and **Li** chains. From triethylamine-catalyzed interfacial phosgenations of bisphenol A[16] and from hydrolytic interfacial polycondensations of BABC[5,9,17] it is well-known that triethylamine generates diethylcarbamate end groups. Furthermore, we have shown in a previous publication[13] that large amounts of diethylcarbamate end groups were formed when bisphenol A was polycondensed with an excess of diphosgene and triethylamine in water-free organic solvents. Therefore, it is not surprising that diethylcarbamate groups were also formed under the reaction conditions of this work as outlined in eqs 3



and 4. The formation of carbamate end groups had the obvious consequence that both chain growth and cyclization were affected. Therefore, a large excess of BABC (7 or 10 mol %) reduced the molecular weight and resulted in larger fractions of **Lg**, **Lh**, and **Lk** chains at the expense of cyclic polycarbonates.

***N*-Ethyl Diisopropylamine (EDPA) as Catalyst.** EDPA, also called "Hünig's Base" is known to be a strong base but a poor nucleophile which for steric reasons does not undergo alkylation in contrast to triethylamine. Hence, it was expected that EDPA does not react with chloroformates to *N*-acylammonium ions so that no carbamate end groups are formed. All polycondensations with EDPA as catalyst were performed analogously to those based on triethylamine, and the excess of BABC was varied. The results compiled in Table 3 indicate that the molecular weights were rather low and did not pass through a maximum. These findings suggested that intensive side reactions had occurred which were confirmed by MALDI−TOF mass spectrometry.

The mass spectra proved the formation cycles as the predominant reaction products below 3000 Da, but numerous mass peaks of linear species were also present. Again, small amounts of chains having one methyl carbonate end group (**Ld**) or two OH end groups (**La**) were detectable. Yet, particularly interesting and conspicuous was the presence of various kinds of linear chains having carbamate end groups. Either these chains contained one carbamate group (**Ll** or **Lm**) or both chain ends consisted of carbamate groups (**Ln**, **Lo**, and **Lp**). This multitude of linear species resulted from the fact that two different types of carbamate groups were present, namely those

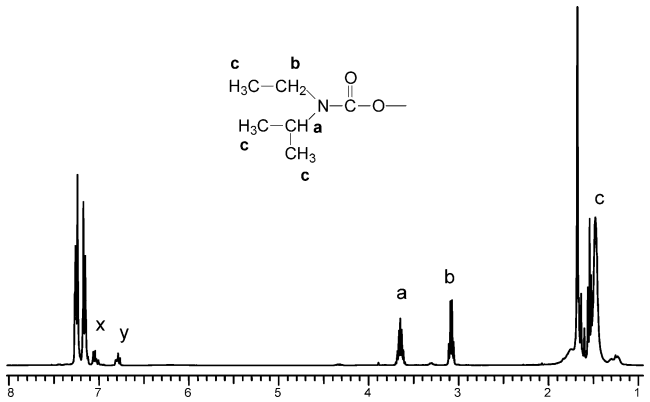
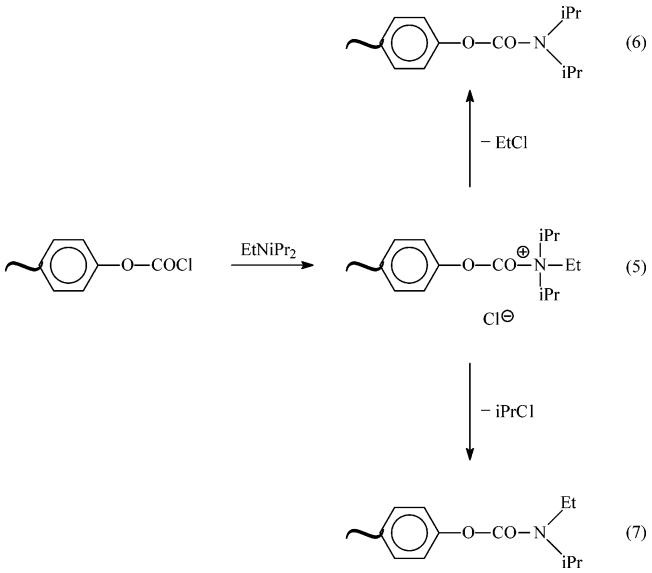


Figure 3. 400 MHz ^{1}H NMR spectrum of a polycarbonate prepared with *N*-ethyl diisopropylamine and 10 mol % excess of BABC (no. 3, Table 3).

based on ethyl isopropylamine and those derived from diisopropylamine. The presence of carbamate end groups containing ethyl and isopropyl groups was confirmed by ^{1}H NMR spectroscopy as illustrated in Figure 3. The content of carbamate end groups varied with the excess of BABC, and passed a maximum for 10% excess. The ^{1}H NMR spectrum of the sample (no. 3, Table 3) is presented in Figure 3. This finding proved against our expectation that EDPA can react with chloroformates, and the intermediately formed acylammonium ion (eq 5) can decompose in two ways (eqs 6 and 7). If this decomposition really involves a formation of alkyl chlorides, as formulated in eqs 6 and 7 is questionable. The predominant elimination of isopropyl groups rather suggests a base-assisted elimination of propene and HCl. A degradation based on the nucleophilic attack of chloride ions onto the alkyl groups of N-acylammonium ions should largely favor the elimination of ethyl chloride. Regardless of the mechanisms, our results prove that EDPA is highly reactive toward chloroformates and far from catalyzing clean polycondensations.



Pyridine-Catalyzed Polycondensations of Sebacoyl Chloride. A few pyridine-catalyzed polycondensations of bisphenol A with sebacoyl cloride were performed for comparison with the polycondensations of BABC presented in Table 1. Pyridine-promoted polycondensations of bisphenol A and sebacoyl chloride have already been described in a previous paper,[18] but the concentrations of the reactants were considerably higher. The results obtained under the reaction conditions characteristic for the present work are summarized in Table 4. The inherent viscosities were comparable to those obtained from BABC and triethylamine (Table 2) and lower than those achieved with BABC and pyridine (Table 1). A maximum molecular weight was obtained with an excess of 2 mol % of sebacoyl chloride (at 1 mol % in the previous study[18]). The consumption of this excess of sebacoyl chloride may be ascribed to traces of moisture or to β-elimination of HCl from the acid chloride groups. In agreement with our theory of kinetically controlled polycondensation, the MALDI−TOF MS revealed that all polyester samples contained sizable amounts of cycles, but the maximum fraction of cycles was found for the sample with the highest molecular weight as evidenced by the MS of Figure 4.

In summary, it was found that the polycondensations of sebacoyl chloride agreed with those of BABC in three important aspects. First, the molecular weights had the same order of magnitude. Second, molecular weights and content of cycles peak for the same sample. Third, under optimum reaction conditions, cyclization is the main limiting factor for the chain growth.

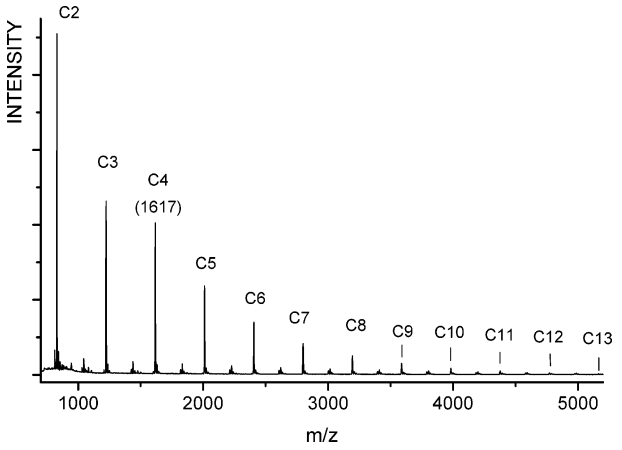
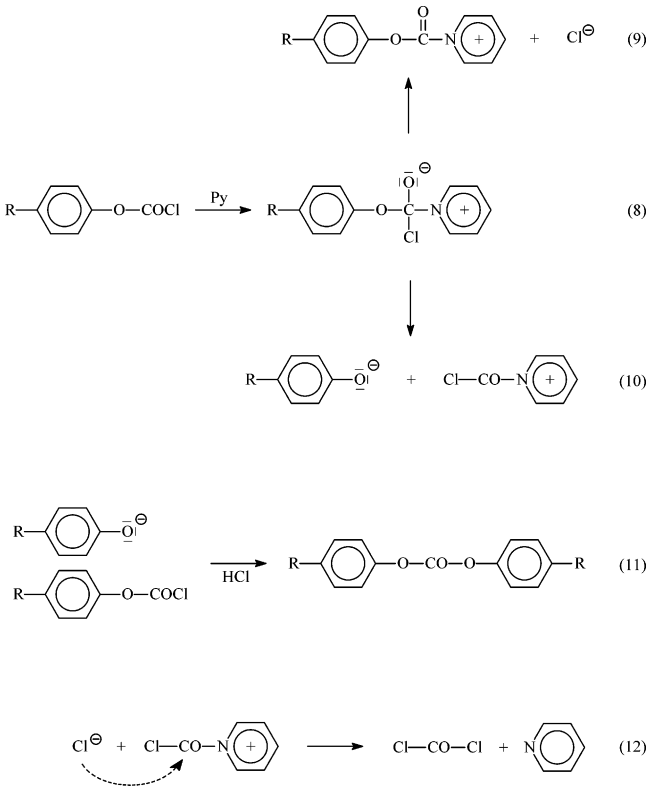


Figure 4. MALDI−TOF MS of the polyester prepared with pyridine and 2 mol % excess of sebacoyl chloride (no. 3, Table 4).

Mechanistic Discussion. The experiments of this work yielded two interesting results which need a more detailed discussion. At first, the side reactions of BABC and the formation of odd-numbered cycles in pyridine-catalyzed polycondensations should be commented. Under optimum conditions, an excess of 10−15 mol % of BABC is consumed without any other side reaction than the formation of odd-numbered cycles. As demonstrated by polycondensations with sebacoyl chloride, moisture may at best account for a consumption of 1−2 mol % of BABC. Therefore, two model experiments were performed. First, phenyl chloroformate was heated with pyridine in refluxing CH_2Cl_2, and after 24 h, crystalline diphenyl carbonate was isolated. Furthermore, neat BABC was heated with pyridine in dichloromethane for 24 h. The solid white reaction product was identified by MALDI−TOF mass spectroscopy as oligocarbonate mainly consisting of OH and methyl carbonate terminated **La**, **Ld**, and **Le** chains. These end groups were formed by hydrolysis and methanolysis from chlorocarbonate groups (**Lb** and **Lc** chains) during the isolation and purification of the oligocarbonate. Yet, interestingly, equal quantities of odd- and even-numbered cyclocarbonates were also found. These results prove that the formation of carbonate groups from chloroformates does not need the presence of phenols or water, and suggest the "disproportionation mechanism" outlined in eqs 8−12. This mechanism explains why optimized polycondensations of bisphenol A and BABC (Table 1) require a considerable excess of BABC and yield odd-numbered cycles as byproducts.

The second point of particular interest is the relatively low molecular weights obtained with pyridine or triethylamine under optimum conditions. From the interfacial hydrolytic polycondensation of BABC, an inherent viscosity of 2.7 dL/g was obtained[10] when triethylamine was used as catalyst representing a factor of 9 relative to the best result of Table 2. With phase transfer catalysts, the highest inherent viscosity amounted to 4.7 dL/g, meaning a factor of 9 relative to the best results obtained with pyridine (Table 1) or a factor of 15 relative to triethylamine (Table 2). Considering that the exponent in the Mark−Houwink equation of polycarbonates amounts to 0.7 in CH_2Cl_2,[10] the molecular weights resulting from interfacial polycondensations were by factors of 12−20 higher than those obtained in this work under homogeneous conditions.



The difference between molecular weights resulting from interfacial phosgenation of bisphenol A, on one hand, and phosgenation in homogeneous organic solution, on the other, was even higher. Optimized interfacial phosgenations of bisphenol A yielded polycarbonates with inherent viscosities in the range of 7−9 dL/g,[15] ($M_n \sim 300-400$ kDa) what means that the molecular weights were by factors of 25−30 higher than those obtained from homogeneous phosgenations ($M_n \sim 9-15$ kDa).[13]

The polycondensations of bisphenol A with sebacoyl chloride presented in this work and in a previous paper[17] prove that the molecular weights obtained with BABC in the monophasic polycondensations are quite normal, whereas the high molecular weights resulting from interfacial polycondensations are unusual. Taking into account that under optimized reaction conditions cyclization is the main limiting factor for the chain growth, these results evidence that the efficiency of cyclization is severely reduced in interfacial polycondensations. This conclusion raises the following question: Why is the exponent "a" in eq 2 significantly higher for interfacial polycondensations? Under homogeneous conditions the reaction mixture of an $a_2 + b_2$ polycondensation contains three species with respect to the end group combination: "a−a chains", "b−b chains", and "a−b chains". Under ideal conditions, their molar ratio is 1:1:2. Since the "a−a" and "b−b chains" can contribute to the chain growth but not to cyclization, 50 mol % of the reaction products (i.e., the "a−b chains") are capable to cyclize. In the case of a hydrolytic interfacial polycondensation of BABC, the phenoxide ions which are gradually generated by the hydrolysis of chloroformate groups are surrounded by a huge excess of chloroformate groups, so that the **Lc** chains having two chloroformate groups largely dominate over the **Lb** chains. Therefore, the fraction of chains that can cyclize is far lower than in the case of a one-phasic polycondensation. Perhaps this "statistical" effect is not the only reason for the reduced efficiency of cyclization in interfacial polycondensations, but it certainly makes a major contribution.

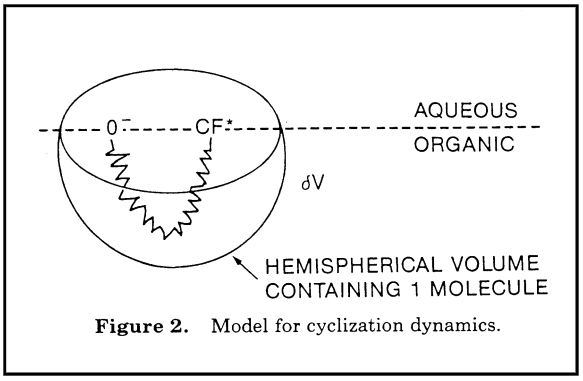


Figure 2. Model for cyclization dynamics.

Figure 5. Mechanistic scheme explaining a selective formation of cyclic oligocarbonates under the conditions of the hydrolytic interfacial polycondensation of BABC. Reproduced with permission from Figure 2 in ref 19. Copyright Wiley 1991.

These results and their interpretation deviate largely from what has previously been published by Brunelle and other members of the GE group. Their first report[7] on the preparation of cyclic oligocarbonates via the hydrolytic polycondensation of BABC using the pseudo-high dilution method, was entitled "Remarkable Selective Formation of Macrocyclic Aromatic Carbonates...". However, any evidence for a remarkable selectivity of this interfacial polycondensation is lacking, inasmuch as the formation of macrocycles under the conditions of the Rüggli-Ziegler dilution principle is quite normal. Furthermore, Kosky[19] proposed a special mechanism explaining the allegedly selective cyclization of oligocarbonates via ionic end groups at the interface (Figure 5). At first, states that ions in contact with water are surrounded by a hydration shell which is lacking in the scheme of Figure 5 (i.e., Figure 2 in ref 19). However, ionic groups react in organic solution several orders of magnitude faster than in their hydrated form in water, and the hydrated acylammonium ion will faster hydrolyze than cyclize. Anyway, this hypothesis of Kosky was an attractive concept at a time when cyclization of polymers was still considered to be an extraordinary reaction. Meanwhile, we have demonstrated for numerous polycondensations that cyclization competes with chain growth at any stage and any concentration.[4] Therefore, a special mechanism explaining the formation of cyclic oligo- and polycarbonates is not needed, and the results of this and a previous study[13] prove that the interfacial method is highly unfavorable for cyclization.

Conclusions

The experiments of this work demonstrate that polycondensations of bisphenol A and BABC are best catalyzed by pyridine, because trialkylamines cause significantly more side reactions. However, pyridine initiates a special side reaction, a so-called disproportionation of chloroformate groups, which has two interesting consequences. A larger excess of BABC is required to optimize the molecular weight and a significant fraction of odd-numbered cycles is formed. Under optimized reaction conditions, the chain growth is mainly limited by cyclization. When optimized polycondensations in a homogeneous phase are compared to interfacial polycondensations of BABC, much higher molecular weights can be achieved by interfacial polycondensation because this biphasic system is unfavorable for cyclization reactions. In contrast, low molar mass cyclic polycarbonates are best synthesized by polycondensations in a homogeneous phase. This conclusion is also valid for polycondensations of bisphenol A with dimeric or trimeric phosgene and it is most likely valid for syntheses of polycarbonates from other diphenols.

Finally, it should be mentioned that the present work and a previous study[13] also serve as a background for analogous polycondensations of other diols. In our current studies of syntheses of polycarbonates it was found that other diols, such as isosorbide, may react quite differently from bisphenol A.

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