Cyclic Polycarbonates by Polycondensation of Bisphenol A with Triphosgene†

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ABSTRACT: Interfacial polycondensations of bisphenol A with triphosgene were conducted in the CH_2Cl_2/aqueous NaOH system. Four different catalysts were compared: triethylamine, triethylbenzylammonium chloride (TEBA-Cl), tetrabutylammonium hydrogen sulfate, and tetraphenylphosphonium chloride. Triethylamine yielded mixtures of cyclic polycarbonates and OH-terminated polycarbonates. The fraction of cycles and the molecular weights increased with lower concentrations of this catalyst. When the pseudo-high-dilution method was applied, samples containing ≥95 mol % of cycles were obtained, and the average molecular weights were varied over a broad range via the feed ratio of triethylamine. Fractionation of one sample allowed the detection of cyclic polycarbonates up to 28 000 Da. The three phase transfer catalysts gave quite different product mixtures when compared under identical conditions. The highest fraction of cycles and the highest molecular weights were obtained with Ph_4PCl. The fraction of cycles increased with higher feed ratios of Ph_4PCl in contrast to triethylamine. Bimodal mass distributions were found for all samples with a high content of cyclic polycarbonates, whereas the frequency distributions were monomodal.

Introduction

The high toxicity of phosgene combined with its gaseous character and a relatively pleasant smell in high dilution renders this versatile reagent a dangerous chemical. Two less dangerous substitutes have been commercialized over the past two decades, namely diphosgene (trichloromethyl chloroformate) and triphosgene (bis(trichloromethyl) carbonate). Whereas diphosgene contains a chloroformyl group like phosgene, triphosgene has a different structure, and thus, the question arises if the reactivity and preparative usefulness of triphosgene are comparable to those of phosgene. In numerous organic syntheses triphosgene has proven its usefulness.[1] Furthermore, numerous polycarbonates were prepared by interfacial polycondensations with triphosgene.[2−5] However, the influence of various catalysts on the course of these polycondensations has never systematically been studied. Another interesting aspect that has not been studied yet is the extent of cyclization in triphosgene-mediated syntheses of polycarbonates.

In a recent study[6] we have found that the results of interfacial polycondensations of bisphenol A by means of diphosgene are highly sensitive to slight variations of the reaction conditions. Careful optimization allows for the preparation of high molar mass polycarbonates with weight-average molecular weights (M_w) above 10^6 Da, unless a chain terminator is used. Furthermore, both molar fraction and ring size of cyclic oligo- and polycarbonates systematically increased with higher molecular weights of the entire sample. This tendency is characteristic for all kinetically controlled polycondensations as recently demonstrated for several different classes of polymers.[7−9] In this context, it was one purpose of the present work to perform interfacial polycondensations of bisphenol A with triphosgene and to study the influence of various catalysts on the efficiency of the chain growth and on the extent of cyclization. Another purpose was the synthesis of cyclic polycarbonates of low or medium molecular weight useful for processing from the melt.

Table 1. Interfacial Polycondensation of BPA with Triphosgene[a] Catalyzed with TEA

expt no.	TEA/BPA	yield (%)	η_{inh}[b] (dL/g)	M_{ei}[c] (Da)	M_v[d]
1	0.5/21	79	2.50	>15 000	130 000
2	1/21	72	2.85	>15 000	140 000
3	2/21	61	2.60	>15 000	135 000
4	4/21	67	0.67	3300	25 000
5	8/21	50	0.25	2000	13 000
6	12/21	41	0.19	1600	12 000

[a] Initial temperature +5 °C, molar NaOH/BPA ratio 126/21 molar triphosgene/BPA ratio 14/21. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] Mass where cyclic and linear polycarbonates show equal peak intensities in the MALDI−TOF MS. [d] Calculated from the η_{inh} values via the MH equation (14).

Experimental Section

Materials. Bisphenol A was a gift of Bayer AG (Leverkusen, Germany) and was used after recrystallization (purity >99% by GC). Triphosgene was purchased from Lancaster Synthesis (Clariant, Frankfurt, Germany) and was used as received. CH_2Cl_2 was also a gift of Bayer AG and was distilled over P_4O_{10} before use. Triethylamine was a gift of BASF AG (Ludwigshafen, Germany) and was used as received. Benzyltriethylammonium chloride (TEBA-Cl), tetrabutylammonium hydrogen sulfate, and tetraphenylphosphonium chloride were all purchased from Aldrich Co. (Milwaukee, WI) and used as received.

Polycondensations. *(A) With Triethylamine (Table 1).* Bisphenol A (21 mmol) and NaOH (126 mmol) were dissolved in H_2O (200 mL) and cooled to +5 °C in a refrigerator. Triphosgene (14 mmol) was dissolved in dry CH_2Cl_2 (200 mL) and cooled to +5 °C. Immediately before both solutions were mixed with a high-speed stirrer ("Ultraturrax"), the triethylamine (2 mmol) was added to the water phase. During the high-speed

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Table 2. Triethylamine-Catalyzed Interfacial Polycondensations[a] of Bisphenol A with Triphosgene via the Pseudo-High-Dilution Method at 20 °C

expt no.	TEA/Bisphenol A	yield (%)	η_{inh}[b] (dL/g)	η_{intr}[c] (dL/g)	M_n[d,e] (Da)	M_w[d] (Da)	T_g[f] (°C)
1	0.25/21	73	1.03	1.08	10 000	95 000	148.5
2	0.50/21	72	1.51	1.53	14 500	175 000	150.5
3	1.00/21	71	0.45	0.48	4 500	36 000	146.0
4	2.00/21	70	0.36	0.37	3 500	28 000	146.0
5	4.00/21	69	0.34	0.35	3 000	26 000	139.5

[a] Initial reaction temperature +5 °C, molar NaOH/BPA ratio 126/21, molar triphosgene/BPA ratio 14/21. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] Measured at 30 °C in CH_2Cl_2. [d] SEC measurements in CH_2Cl_2 evaluated with a triple detector. [e] Because of the broad bimodal MWD the margin of error is on the order of ±15−20%. [f] DSC measurements with a heating rate of 20 °C/min (first heating).

Table 3. Characterization of the Ten Fractions Obtained by SEC from Sample No. 3, Table 2

		SEC measurements		
no.	$[\eta]$[a] (dL/g)	M_w[b]	M_p[c]	MALDI-TOF M_p[d]
1	2.143	260 000	243 000	
2	1.508	135 000	122 000	
3	0.943	66 000	62 000	
4	0.557	33 500	32 000	29 000
5	0.327	21 000	19 500	14 300
6	0.243	12 500	11 200	7 400
7	0.102	8 100	6 200	3 300
8				1 560
9				1 050
10				<800

[a] Intrinsic viscosity measured at 30 °C in CH_2Cl_2. [b] Weight-average molecular weight as determined by triple detection. [c] Molar mass of the MWD maximum. [d] Molar mass of the MWD maximum.

stirring, the reaction vessel was cooled with an ice/NaCl mixture. After high-speed stirring for 15 min, the internal temperature had reached values in the range 12−15 °C for almost all polycondensations. The stirring was continued without cooling for 45 min using a normal flat-blade stirrer. The CH_2Cl_2 phase was diluted with 100−500 mL of CH_2Cl_2 (depending on the viscosity) separated from the water phase and washed three times with water. After drying with Na_2SO_4, the CH_2Cl_2 solution was concentrated to approximately 100 mL and precipitated into methanol. The isolated polycarbonate was dried at 80 °C in vacuo.

All other polycondensations based on triethylamine as catalysts were conducted analogously.

(B) Pseudo-High-Dilution Method (Table 2). Bisphenol A (21 mmol) and NaOH (126 mmol) were dissolved in H_2O (150 mL) and thermostated to 19.5−20 °C. Triphosgene (14 mmol) was dissolved in dry CH_2Cl_2 (150 mL). Both solutions were added dropwise and simultaneously to a mixture of 100 mL of H_2O containing NaOH (10 mmol) and CH_2Cl_2 (100 mL) containing triethylamine (1 mmol). During the addition (60 min) the temperature rose to 22 °C. The stirring was continued for 10 min after complete addition. The CH_2Cl_2 was then separated and washed twice with 0.1 N hydrochloric acid and three times with water. Finally, the CH_2Cl_2 solution was dried over Na_2SO_4 concentrated and precipitated into methanol.

(C) With Ph_4PCl (Table 4). Bisphenol A (21 mmol) and NaOH (126 mmol) were dissolved in water (200 mL) and cooled to +5 °C. Triphosgene (14 mmol) was dissolved in dry CH_2Cl_2 (200 mL) and also cooled to +5 °C. Ph_4PCl (4 mmol) was added to the NaOH solution immediately before both solutions were mixed with a high-speed stirrer. The polycondensation was continued as described for (A).

Analogous polycondensations were conducted with TEBA-Cl (4 mmol) or tetrabutylammonium (the MALDI−TOF spectra are presented in Figure 4).

All polycondensations were worked up in such a way that the interlayers of the CH_2Cl_2/H_2O solutions were discarded to obtain NaCl-free polycarbonates for optimum MALDI−TOF measurements. When the interlayers were combined with the CH_2Cl_2 phase and when drying with Na_2SO_4 was avoided, the yields were above 90%. The MALDI−TOF mass spectra in principle agreed with those obtained from products of the standard workup procedure, but strong peaks of Na^+-doped products were present in addition to the K^+-doped peaks with the consequence of lower signal-to-noise ratios.

Table 4. Interfacial Polycondensation of BPA[a] with Triphosgene Catalyzed by TEBA-Cl, Bu_4N-HSO_4, and Ph_4P-Cl

expt no.	catalyst	cat/BPA	yield (%)	η_{inh}[b] (dL/g)	M_{ei}[c]
1	TEBA-Cl	4/21	65	0.53[d]	1000
2	$Bu_4N{\cdot}HSO_4$	4/21	80	0.31	
3	Ph_4P-Cl	1/21	60	0.30	4300
4	Ph_4P-Cl	2/21	50	0.35	4700
5	Ph_4P-Cl	4/21	63	0.42[e]	4900
6	Ph_4P-Cl	8/21	55	0.54	5700
7	Ph_4P-Cl	12/21	51	0.76[f]	>8000

[a] Initial temperature +5 °C, molar NaOH/BPA ratio 126/21, molar triphosgene/BPA ratio 14/21. [b] Measured at 20°C with c = 2 g/L in CH_2Cl_2. [c] Mass where cyclic and linear polycarbonates display equal peak intensities in the MALDI−TOF MS. [d] M_n = 11 100 Da, M_w = 33 000 Da by SEC with triple detection. [e] M_n = 7000 Da, M_w = 29 000 Da by SEC with triple detection. [f] M_n = 17 000 Da, M_w = 55 000 Da by SEC with triple detection.

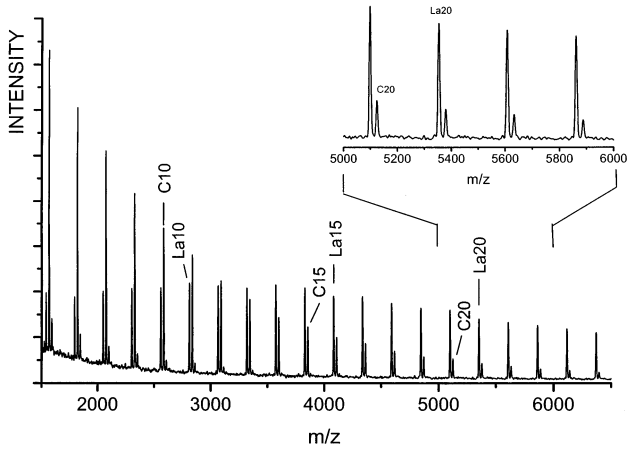


Figure 1. MALDI−TOF mass spectrum of the polycarbonate no. 4, Table 1.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an Ubbelohde viscometer thermostated at 20 °C.

The MALDI−TOF mass spectra were recorded with a Bruker Biflex III equipped with a nitrogen laser (λ = 337 nm) in the reflectron mode. An acceleration voltage of 20 kV and cutoff range of 1000 or 4000 Da were used. The irradiation targets were prepared from CH_2Cl_2 solutions with dithranol as matrix and K-trifluoroacetate as dopant. The SEC were performed on a Hewlett-Packard HP 1050 apparatus in CH_2Cl_2 at 30 °C. Five Lichrogel columns having pore sizes of 4, 40, 400 (2×), and 4000 Å were used. The elution curves were evaluated with a triple detector "Viskotek-TDA 301" combined with the software "Viskotek Tri SEC".

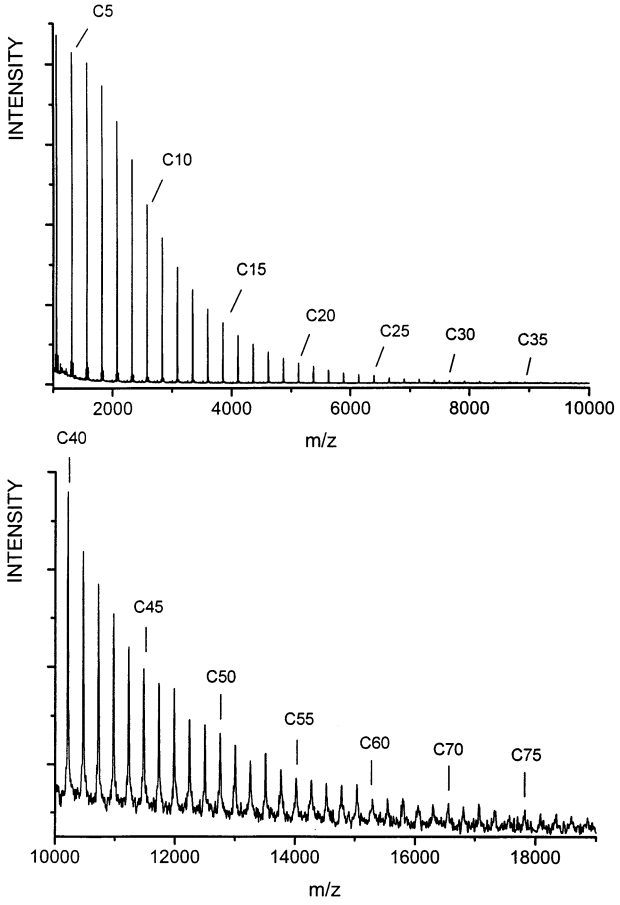


Figure 2. MALDI−TOF mass spectrum of the polycarbonate no. 3, Table 2, prior to its fractionation.

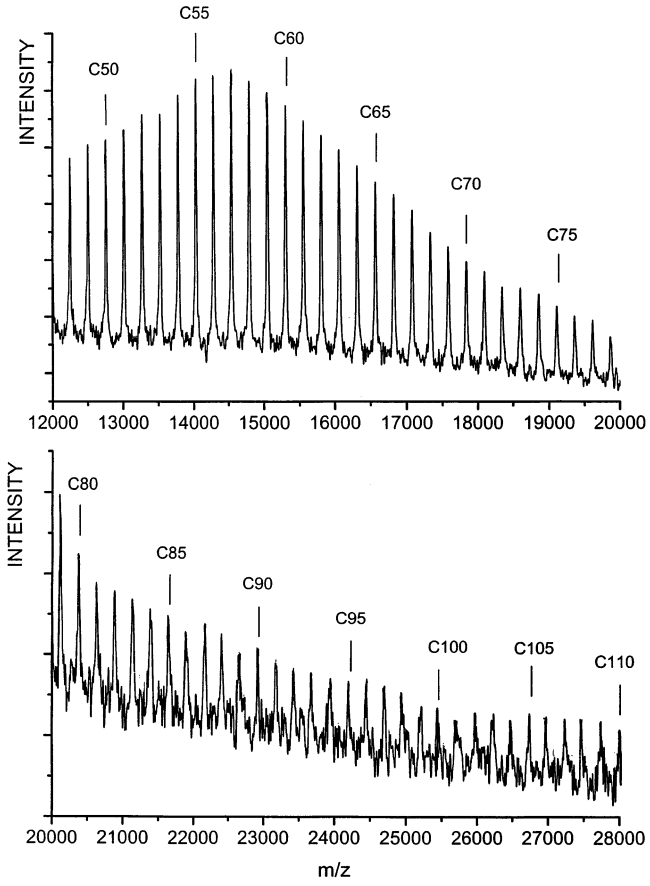


Figure 3. MALDI−TOF mass spectrum of fraction no. 5 of polycarbonate no. 3, Table 2.

Results and Discussion

Triethylamine (TEA) as Catalyst. In a first series of polycondensations TEA was used as catalyst because this amine had proven to be particularly useful in syntheses of cyclic oligo- and polycarbonates via hydrolytic polycondensation of bisphenol A bis(chloroformate).[10−13] Furthermore, TEA has also proven its usefulness in previous studies of interfacial phosgenations of bisphenol A with diphosgene.[5] The reaction conditions were selected to match those used in a previous study based on phosgenation with diphosgene. The molar ratio of triphosgene/BPA corresponded to a 100% molar excess of $COCl_2$, and the NaOH/BPA ratio was designed for complete neutralization of the liberated HCl and 50% neutralization of H_2CO_3. Since an initial temperature below 20 °C has proven to favor propagation and cyclization over hydrolysis of (di)phosgene,[6] the initial temperature used in this work for the first series of experiments (Table 1) was again fixed at +5 °C.

Whereas all these parameters were kept constant, the TEA/BPA ratio was varied. The results listed in Table 1 demonstrate that the inherent viscosities pass through a maximum at a low TEA feed ratio. An analogous trend was found for phosgenations with diphosgene.[6] Even the yields follow this trend, although the workup procedure was not optimized for high yield but for Na-free polycarbonates. Na-free polymers were desirable to obtain optimum MALDI−TOF mass spectra (MS) with K^+ doping.

The MALDI−TOF MS revealed the existence of cyclic polycarbonates in all samples (nos. 1−6, Table 1). When the molecular weight was high, only mass peaks of cycles were detectable (nos. 1−3). Their fraction decreased with lower molecular weights, and the linear chains of structure **La** (Scheme 1) became the predominant reaction products. This trend is illustrated in Figure 1 and by the M_{ei} values listed in Table 1. M_{ei} means the mass value where the mass peaks of cycles and linear chains have equal intensities. Lower M_{ei} values mean lower content of cyclic oligo- and polycarbonates.

The finding that higher molecular weights are combined with higher fractions of cycles is in perfect agreement with our recent theory of step-growth polymerization.[7−9] These results also provide a clue to the polymerization mechanism (together with the results obtained from phase transfer catalysts below). Considering the well-known[14−17] complexation of chloroformate groups with triethylamine, it may be assumed that triethylamine reacts with triphosgene according to eq 1 (see Scheme 2). The acylammonium ion **1** is hydrophilic; it will diffuse into the water phase and hydrolyze (eq 2). Alternatively, it will react with phenoxide ions or with phenol groups (eq 3). The resulting mixed carbonate can react with a phenoxide ion (eq 4) to yield a stable carbonate group (eq 5). Another reaction sequence will start out from the decomposition of the trichloromethoxide ion into chloride ions and phosgene (eq 6). The phosgene will be activated by triethylamine (eq 7), and the acylammonium ion **2** which is more hydrophilic than **1** has in turn the choice between hydrolysis and formation of a phenyl chloroformate group (eq 8). This chloroformate group can react with a phenoxide ion yielding a stable carbonate (eq 9). On the other hand, an activation of the chloroformate with TEA

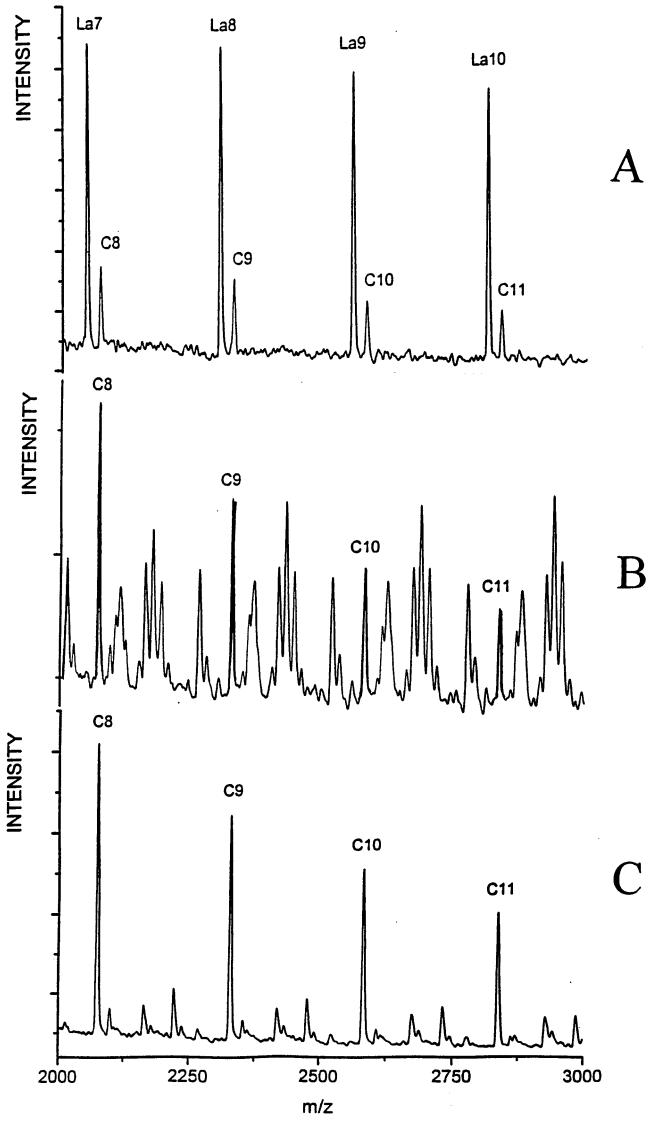
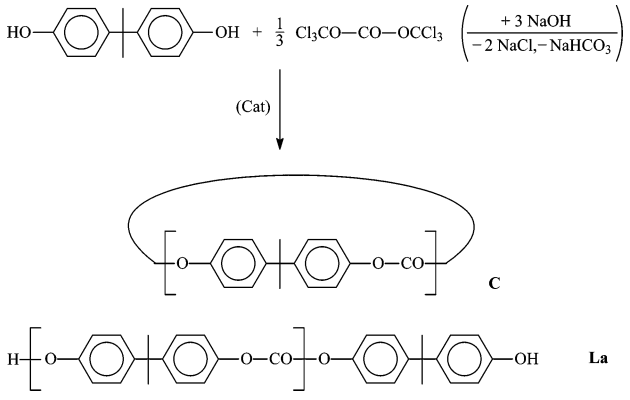


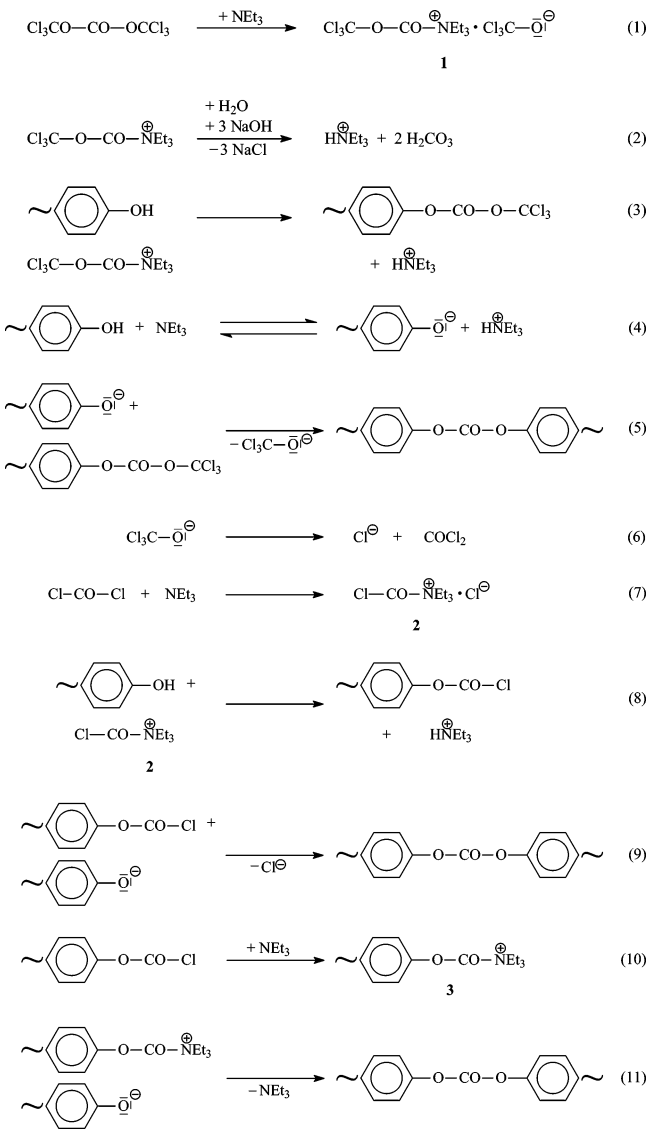
Figure 4. MALDI−TOF mass spectrum of the polycarbonate no. 1, Table 4 (A), no. 2, Table 4 (B), and no. 5, Table 4 (C).

Scheme 1



may take place (eq 10), and the acylammonium ion **3** has then the choice between hydrolysis and continuation of the chain growth (eq 11). Even though eqs 1−11 are not an exhaustive description of all possible reaction steps, they illustrate the role of TEA. The experimental results indicate that higher feed ratios of TEA favor the hydrolysis of triphosgene (and its reaction products) via hydrophilic acylammonium ions more than chain growth and cyclization.

Scheme 2



TEA and the Pseudo-High-Dilution Method. The results discussed above and those obtained with diphosgene[6] have demonstrated that polycarbonates with a high percentage of cycles can be prepared when the reaction conditions favor high molecular weights (weight-average molecular weights, M_ws, in the range 10^5−10^6 Da). However, polycarbonates having M_ws above 50 000 Da possess too high a melt viscosity for processing. Therefore, it was of interest to find reaction conditions allowing for the synthesis of low molar mass cyclic polycarbonates. For this purpose, a second series of polycondensations were conducted using the pseudo-high-dilution method in combination with a higher reaction temperature. The feed ratio of TEA was varied, whereas all other parameters were kept constant.

The results summarized in Table 2 allow the following conclusions. First, the molecular weights pass through a maximum around 2.5 mol % of TEA (relative to BPA). Compared to the polycondensations performed at higher concentrations (Table 1), the maximum of the molecular weights is shifted to a lower feed of TEA. Second, all molecular weights are shifted to lower values as expected for the pseudo-high-dilution method. However, at the optimum TEA feed, the molecular weight of the isolated polycarbonate (no. 2, Table 2) is still too high

for a convenient processing. Third, the most interesting and important result is the observation that the MALDI−TOF MS of all samples are nearly identical, despite a broad variation of the molecular weights. Even in the case of sample no. 4 (Table 2) only traces of linear chains (**La** type) are detectable, whereas no linear chains were found at masses above 3000 Da. This trend is quite different from that found for the samples of Table 1 as illustrated by a comparison of the MS presented in Figures 1 and 2. This comparison demonstrates that the pseudo-high-dilution method favors the cyclization even at low molecular weights.

The MS presented in Figure 2 demonstrates that the signal-to-noise ratio is poor above 10 000 Da. To obtain more information about the structure of the polycarbonate chains above 10 000 Da, sample no. 3, Table 2, was fractionated by SEC, so that 10 fractions were obtained. The characterization of these fractions is summarized in Table 3. These fractions were characterized by MALDI−TOF mass spectrometry, and from five fractions satisfactory mass spectra were obtained, whereas in the case of fraction 4 the signal-to-noise ratio was poor. In all MS, only mass peaks of cyclic oligo- and polycarbonates were observable. The best mass spectrum is displayed in Figure 3. Cyclic polycarbonates were detectable up to 28 000 Da. Considering the relatively low M_n and M_w values of this sample, it may be concluded that certainly more than 90 mol % of this sample consists of cycles. (The weight percentage is necessarily lower than the mole percentage because the longest chains have the lowest tendency to cyclize.) This estimation is based on the following consideration: The majority of cycles (around 65−70 mol %) is concentrated in the mass range of the frequency distribution below M_n. Around 90 mol % are concentrated in the mass range of the frequency distribution below M_w. Furthermore, the M_n and M_w values obtained by triple detection overestimate the true molecular weights in the mass range below 30 000 Da, as evidenced by a comparison of MALDI−TOF and SEC measurements of the fractions listed in Table 3. The reason for this discrepancy is the fact that the absolute molecular weights of the triple detection are based on light scattering, which is insensitive to the presence of (cyclic) oligomers and low molar mass polymers. For the other samples listed in Table 2, a similarly high content of cyclic oligo- and polycarbonates may be assumed as for no. 3. Therefore, these results prove that triphosgene is particularly well suited to prepare cyclic polycarbonates with variable molecular weights by direct polycondensation of bisphenol A.

Considering that the content of cycles is quite similar in all four samples of Table 2, these samples are well suited to study the dependence of chemical and physical properties on the molecular weight. In this work, only glass transition temperatures (T_gs) should be reported which play a key role for the heat distortion temperature and thus for commercial applications of the polycarbonate. The T_gs listed in Table 2 display the expected dependence on the molecular weight, but a significant deviation from the T_gs of commercial linear polycarbonates having similar molecular weights was not detectable.

Phase Transfer Catalysis. The successful use of phase-transfer (PT) catalysts in the interfacial phosgenation of various diphenols by means of monomeric phosgene is well documented in the literature.[18,19] In a previous study[6] based on diphosgene triethylbenzylammonium chloride (TEBA-Cl) and tetrabutylammonium (TBA) hydrogen sulfate were used. Both PT catalysts gave similar results. The content of cyclic polycarbonates increased with higher molecular weights of the reaction products. In the present work, these PT catalysts were again used, and tetraphenylphosphonium (TPP) chloride was also included in this study.

All three PT catalysts were compared under identical conditions (nos. 1, 2, 5; Table 4), and these reaction conditions corresponded to the standard conditions also used for the experiments of Table 1. Surprisingly, three different reaction products were obtained as evidenced by the MALDI−TOF MS presented in Figure 4. With TEBA-Cl only few cycles were formed, and the vast majority of the products consisted of linear chains having two OH end groups (**La**). In the original MS, the mass peaks of these **La** chains were detectable up to 18 000 Da. In the case of TBA hydrogen sulfate, a variety of different products were formed which were

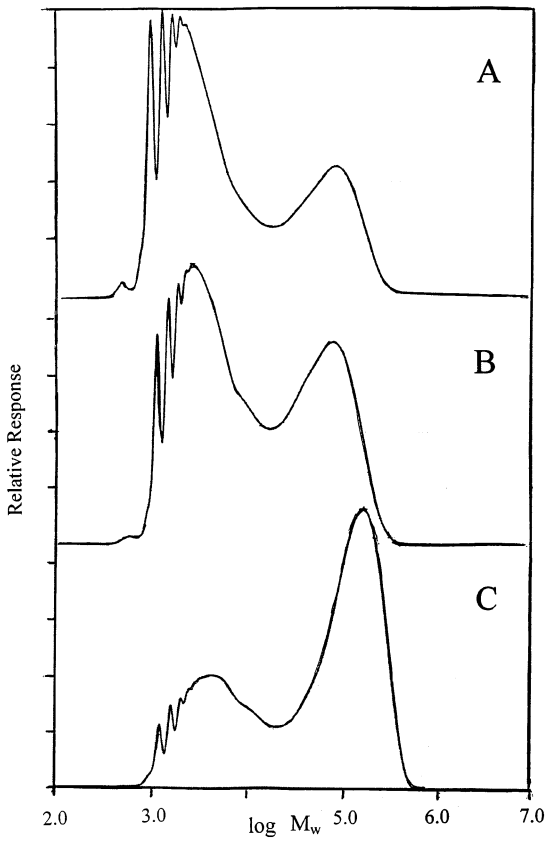
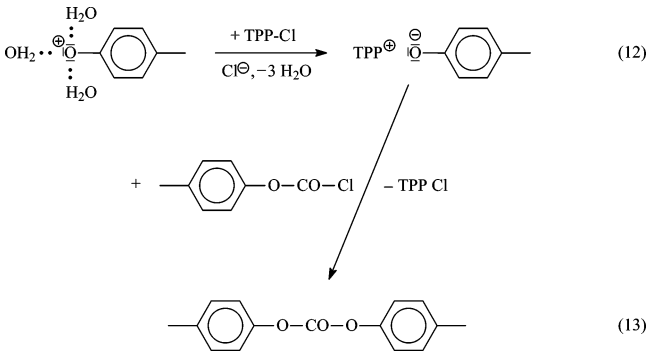


Figure 5. SEC elution curves of the polycarbonates no. 4, Table 2 (A), no. 3, Table 2 (B), and no. 1, Table 2 (C).

Scheme 3



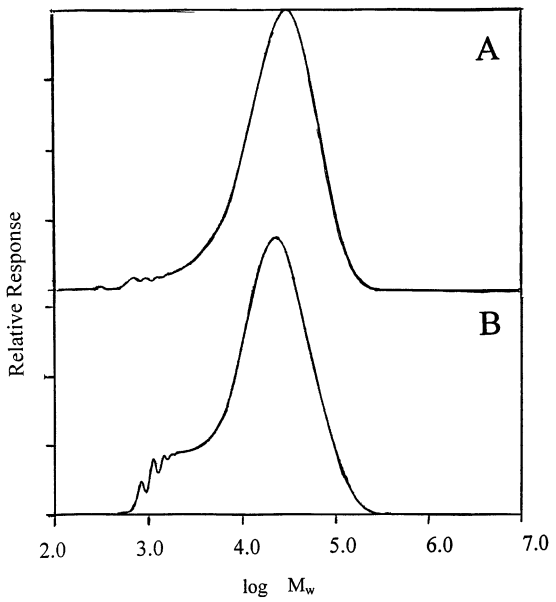


Figure 6. SEC elution curves of the polycarbonates no. 1, Table 4 (A), and no. 5, Table 4 (B).

not analyzed in detail. With TPP-Cl mainly cyclic oligo- and polycarbonates were formed. When compared to the TEA-catalyzed sample no. 5 of Table 1, the content of cycles was even higher in the case of the TPP-Cl catalysis.

Particularly interesting proved the trend observed for the variation of the TPP-Cl/BPA ratio. A higher feed of TPP-Cl gave higher molecular weights in combination with a higher content of cycles. This trend is opposite to that found for TEA (Tables 1 and 2), indicating another polymerization mechanism. It is obvious that TPP-Cl (like other PT catalysts) cannot activate triphosgene, phosgene, or chloroformate groups in a manner analogous to TEA (eqs 1, 7, and 10). Hence, the catalytic effect of TPP-Cl must be due to an activation of the phenoxide ion. Besides fluoride ions, oxide ions are the strongest acceptors of H-bonds and, therefore, surrounded by a rather stable shell of H_2O molecules when dissolved in water. The transfer to the organic phaseremoves most or all of the water molecules, as schematically outlined in eq 12 (see Scheme 3). This change of the solvation shell tremendously enhances the nucleophilicity, and this change is the basis of phase-transfer catalysis.[20,21]

The TPP cation will also transfer more or less hydrated OH^- ions to the organic phase,[21] thereby catalyzing the hydrolysis of triphosgene, phosgene, and chloroformate groups. However, the phenolic OH groups are about 6 orders of magnitude more acidic than water, so that the concentration of phenoxide groups in the organic phase should be much higher than that of hydroxide ions. In consequence, increasing feed ratios of TPP-Cl favor propagation (eq 13) and cyclization over hydrolysis of the electrophilic reaction partners. A similar trend was observed for TEBA-Cl when diphosgene was polycondensed with bisphenol A.[6]

In summary, the results obtained in this work demonstrate that the structure of the PT catalyst has an enormous influence on the composition of the reaction product. Furthermore, the reactivity of triphosgene toward PT catalysts is different from that of diphosgene and thus justifies a separate investigation.

Molecular Weight Distributions (MWDs). In our previous work on polycarbonates,[6] a Mark−Houwink−Sakurada equation

$$[\eta] = 0.036 M_w^{0.70} \tag{14}$$

was elaborated for polycarbonates of bisphenol A mainly consisting of cycles. This equation was used to calculate the viscosity-average molecular weights listed in Table 1 which had the purpose to illustrate the order of magnitude. These M_v values were calculated from the inherent viscosities which usually deviated from intrinsic viscosities by 5% as found by comparison of numerous viscosity measurements.[6,13,22] A higher accuracy of the M_v calculations is not more informative because the MWDs vary with the reaction conditions as demonstrated below and in a previous publication.[6]

Samples nos. 1−5 of Table 2 and nos. 1 plus 5 of Table 4 were subjected to SEC measurements which were evaluated by the triple-detection method including light scattering. The samples of Table 2 displayed a bimodal mass distribution regardless of their molecular weight (Figure 5). Similar bimodal mass distribution were found in previous studies[13] of hydrolytic polycondensation of bisphenol A carbonate, whenever high fractions of cycles were formed. Similar bimodal mass distributions were also observed for syntheses of poly(ether sulfone)s under conditions favoring the formation of cycles.[23] Hence, it may be concluded that the bimodal mass distribution is not a consequence of the interfacial polycondensations. This conclusion is supported by the results obtained with PT catalyst. With TEBA-Cl (no. 1, Table 4) only few cycles were formed (Figure 4A), and the SEC curve (Figure 6A) displays a monomodal character. Under the same conditions Ph_4PCl yielded a much higher fraction of cycles (Figure 4C), and the SEC curve displayed a "bimodal trend" (Figure 6B). These bimodal MWDs have, of course, the consequence of high polydispersities, and the margin of error of the number-average molecular weights (M_ns) is particularly large.

The relationship between permanent cyclization and bimodal mass distribution can be rationalized considering that the cylic oligomers mainly formed in an early stage of a polycondensation are stable under the conditions of a KCP and do not vanish. In contrast, Flory's original concept of step-growth polymerizations[24] does not include a significant contribution of cyclization reactions and predicts a monomodal mass distribution according to the equation

$$W_n = mp^n(1 - p) \tag{15}$$

where W_n = (weight fraction of oligomers)/(polymers having a degree of polymerization n), m = molar mass of the repeating unit, and p = conversion. This concept is based on the assumption that all (linear) oligomers gradually vanish with increasing conversion. The results presented here and in other recent publications clearly prove that kinetically controlled polycondensations do not obey Flory's original treatment of MWDs. However, it should also be mentioned that Flory calculated later[25] a bimodal mass distribution for thermodynamically controlled polycondensations involving a formation of cyclic oligomer via "backbiting" equilibration. This later modification of Flory's theory may be considered as an indirect confirmation of our hypothesis that when

intensive cyclization occurs in a KCP a bimodal mass distributions will result.

Conclusion

The results elaborated in this work allow interesting conclusions in three directions. First, the reactivity of triphosgene is so different from that of diphosgene that at least with PT catalysts interfacial polycondensations of diphenols give results which are quite different from those obtained with diphosgene under identical conditions.[5,21] Second, triphosgene allows one to prepare cyclic oligo- and polycarbonates of bisphenol A in a simple "one-pot-procedure" based on the pseudo-high-dilution method and triethylamine as catalyst. Variation of the catalyst feed and of the temperature (documented in more detail in a future publication) allows one to vary the average molecular weight of the cyclic polycarbonates over a broad range. Third, the SEC elution curves prove together with those recently obtained from other polymer syntheses[12,21,22] that reaction conditions yielding a high percentage of cycles automatically produce a bimodal mass distribution along with a monomodal frequency distribution. These MWDs differ from those calculated by Flory[25] in his classical theory for polycondensations, where a significant influence of cyclization reactions on kinetically controlled polycondensations was not taken into account. Further studies designed to elucidate both the experimental and the theoretical background of MWDs of cyclic polymers are in progress.

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