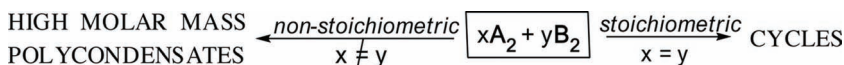


# Non-Stoichiometric Polycondensations and the Synthesis of High Molar Mass Polycondensates

Hans R. Kricheldorf,\* Mikhail G. Zolotukhin, Jorge Cárdenas

This report presents a general overview of non-stoichiometric step-growth polymerizations (polycondensations). Three kinds of non-stoichiometric polycondensations are defined and discussed for  $a_2 + b_2$  monomer combinations. Depending on the kinetic scenario and on the experimental conditions, the excess of one monomer either strongly reduces or strongly enhances the average degree of polymerization (DP) relative to a stoichiometric polycondensation under identical conditions. As a result, telechelic oligomers or extremely high molar mass polymers (DPs > 1000) may be formed. Stoichiometric imbalance has in all cases the consequence that cyclization is largely suppressed in early stages of a polycondensation. Finally, non-stoichiometric “ $a_2 + b_n$ ” polycondensations are discussed.



## 1. Introduction

Polycondensations may be subdivided into two groups according to the structure of the monomers, namely into **a-b** monomers and into  $a_2 + b_2$  monomer combinations. As pointed out in a previous review article<sup>[1]</sup> both systems differ largely in various aspects. Polycondensations of **a-b** monomers exclusively yield oligomers and polymers having one “a” and one “b” chain end, so that cyclization can efficiently compete with chain growth. If the monomers react faster with each other than with oligomers and polymers, or if the monomers react slower with each other, has no influence on the cyclization tendency ( $V_{cy}/V_{pr}$ ) or on the final DP.

For polycondensations of  $a_2 + b_2$  monomers three different scenarios may be defined:

- I) Monomers, oligomers and polymers possess nearly identical reactivities. Chains having two “a”, two “b” or one “a” and one “b” end group are present, and in the case of ideal stoichiometry their molar ratio will be 1:1:2. This is the normal or standard case of an “ $a_2 + b_2$ ” polycondensation.
- II) The monomers react faster with each other than with oligomers and polymers. In this case a relatively high concentration of dimers will be formed in the beginning, but the further course of the polycondensation resembles the standard case I.
- III) The reaction of one monomer (say  $b_2$ ) with monomer  $a_2$  or with “a” end groups is slower than the growing steps of the “b” end groups. In other words, the “b” end groups are activated relative to monomer  $b_2$ . The fast reactions of “b” end groups with  $a_2$  monomers have the consequence that oligomers and polymers having two “a” end groups prevail in the reaction mixture. This scenario is usually called non-stoichiometric polycondensation in a narrower sense, because the addition of excess  $b_2$  monomer accelerates the polycondensation and yields higher DPs.

A non-stoichiometric monomer mixture may also be used in the standard case I. Here, an excess of  $b_2$  reduces

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the DP and produces an excess of chains having two “b” end groups. Such a polycondensation is of interest for the preparation of telechelic oligomers and polymers (type Ia). In contrast to the non-stoichiometric polycondensation of Type III, an excess of  $b_2$  has the consequence that oligomers having two “b” end groups prevail in the reaction mixture and the DP is kept low. However, standard polycondensations may also be performed in such a way that the monomer used in excess (say  $b_2$ ) is gradually removed from the reaction mixture (e.g., by distillation, Type Ib) or by side reaction (Type Ic). In the text below, the discussion is focused on the role of the cyclization reaction, because this aspect is fundamental to the proper understanding of non-stoichiometric polycondensations and because this aspect has never been discussed before. In addition to literature data, new results from the polycondensations of isophthaloyl chloride and 1,6-hexanediol or two bisphenols will be considered. Finally, the influence of non-stoichiometric feed ratios on the course of “ $a_2 + b_n$ ” polycondensations is described. Again cyclization plays a decisive role in the successful syntheses of soluble reaction products and in their architecture.

## 2. Results and Discussion

### 2.1. Type I Polycondensations

#### 2.1.1 Polyester Syntheses in Bulk

Syntheses of polyesters and polyamides by  $a_2 + b_2$  polycondensations in bulk (i.e., in the melt) were first studied by Carothers and co-workers in the years 1930–1935.<sup>[3–10]</sup> After they had learned how to remove the water efficiently from the molten reaction mixture, they prepared the first high molar mass polyesters and polyamides (number average molar masses,  $\bar{M}_n > 12\,000$  Da), and thus the first man-made fibers. In contrast to all the other polycondensations described in the following sections, these polycondensations involve rapid equilibration reactions and may be called thermodynamically controlled polycondensations. These equilibrations are ester-ester interchange and transamidation reactions respectively, on the one hand, and the formation of cycles by “back-biting”, on the other.

The historic syntheses of polyamides and the modern production of Nylons are based on perfectly stoichiometric monomer combinations. Non-stoichiometric polycondensations have not attracted any interest in the field of polyamides. The situation may be different in the case of polyesters depending on the volatility of the diols. When long aliphatic diols of low volatility are used, relatively high molar mass polyesters may be obtained from stoichiometric monomer mixtures. Carothers and co-workers indeed prepared their first “superpolyesters”



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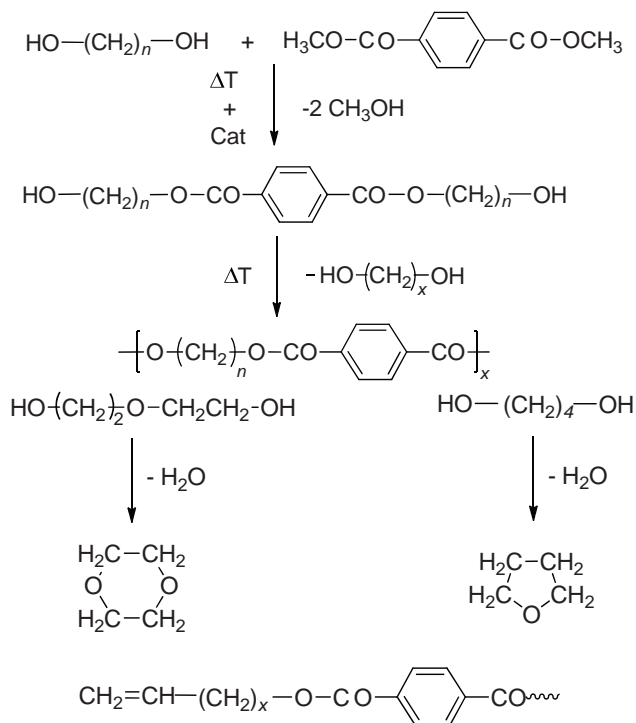
**Mikhail Zolotukhin** obtained his BSc in Chemistry (1974) from Ufa Technical University (Russia), and his PhD (1980) and his degree of Doctor of Science (Chemistry) (1997) from the Institute of Organic Chemistry of Russian Academy of Sciences (Ufa branch). He continued research work at the Institute of Organic Chemistry as a Senior Research Scientist and later as a group leader. In 2003, he joined Instituto de Investigaciones en Materiales of Universidad Nacional Autónoma de México, where presently he is Investigador Titular C, Head of Polymer Department. His current interests include the development of new polymer-forming reactions, syntheses and applications of functional polymers.



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in this way. However, when relatively volatile diols, such as ethanediol, 1,3-propanediol or 1,4-butanediol, serve as monomers, a significant excess (up to 100% or more) is typically used to avoid an excess of the less volatile dicarboxylic acids in the reaction mixture due to distillation of the diol. However, when relatively volatile dimethyl esters of aliphatic dicarboxylic acids are used as the reaction partners of diols, equimolar monomer mixtures may again be the optimum stoichiometry.

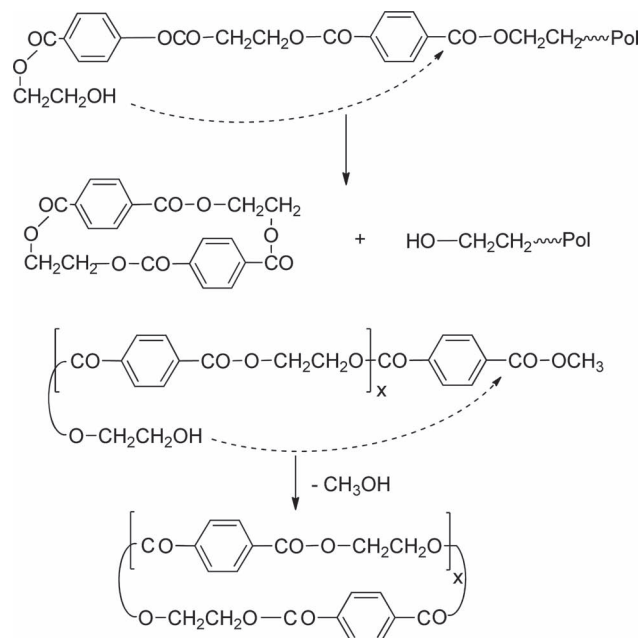
In the case of terephthalic acid, the dimethyl ester is condensed with an excess of the more volatile diols, with



**Scheme 1.** Synthesis of poly(alkylene terephthalate)s and potential side reactions.

the consequence that below 200 °C bis(*o*-hydroxyalkyl) terephthalates are formed as the first reaction products (Scheme 1). The isolation and properties have been described in the literature.<sup>[11–13]</sup> The excess of diols serves not only the purpose of compensating for the loss by distillation, it has also to compensate for the loss by side reactions. The three most frequent and well documented side reactions are, first, the formation of linear ethers such as di(ethylene glycol); second, the formation of cyclic ethers such as dioxane or tetrahydrofuran (Scheme 1); and third, the *cis*- $\beta$ -elimination yielding unsaturated chain ends (Scheme 1). The cyclization is typical for 1,4-butane-diol and the  $\beta$ -elimination most frequently occurs in polycondensations of ethanediol.

Due to the rapid transesterification reactions (Scheme 2) that may occur in these systems, cyclic oligoesters are formed by back-biting. Furthermore cyclic polymers may result from end-to-end cyclization (end-biting). In previous publications, attempts were made to determine the frequency and ring size of cyclic oligo(ethylene terephthalate)s by extraction.<sup>[14,15]</sup> Cyclic oligoesters having a DP up to 5 were isolated and the authors believed that a quantitative extraction of the cycles was achieved. However, extraction is a nice method to separate oligomers from polymers, but not for the separation of cyclics from linear polymers. As demonstrated for Nylons, the quantitative extraction of



**Scheme 2.** Back-biting and end-biting in syntheses of poly(ethylene terephthalate).

cycles is not feasible when the polymers contain cycles with masses > 1000 Da.<sup>[16,17]</sup> Unfortunately, good MALDI-TOF mass spectra of PET, PPT and PBT are relatively difficult to measure. However, at least one MALDI-TOF mass spectrum of a PBT sample with a mass range > 10 000 Da has been reported,<sup>[18]</sup> and the cycles were the prevailing species up to 12 000 Da. This result clearly demonstrates that the formation of cyclics is not limited to low oligomers. Due to cyclization and side reactions, it is difficult to prepare poly(alkylene terephthalate)s having  $\bar{M}_n > 15\,000$  Da, even when the excess of the diol is quantitatively removed.

In this regard the production of aromatic polycarbonates by the transesterification of diphenols with diphenylcarbonate in the melt should be mentioned.<sup>[19]</sup> These polycondensations are conducted with an excess of diphenylcarbonate in the first stage of the process, and the desired DP is controlled by the gradual removal of phenol by distillation. On the one hand, this type of transesterification involves less side reactions than the syntheses of PET or PBT, but, on the other hand, extremely high molar mass polycarbonates are not needed by the chemical industry.

Whereas it is intended in most technical syntheses of PET, PPT and PBT to achieve high molar mass polyester, the technical production of aliphatic polyesters with an excess of diol is aimed at telechelic polymers having two CH<sub>2</sub>OH end groups. A typical example (seemingly the oldest one) is poly(1,6-hexanediol adipate) which has been produced since World War II by Bayer AG. Due

$N_A$  = total number of **A** monomers initially present,  
 $N_B$  = total number of **B** monomers initially present.

$$r = N_A/N_B$$

$p$  = conversion of **A** monomers.

The total number of repeat units is given by

$$(N_A + N_B)/2 = N_A (1 + 1/r) / 2$$

The total number of chain end can be expressed as

$$2N_A(1 - p) + (N_B - N_A) = N_A [\Sigma (1 - p) + (1 - r)/r]$$

This must equal twice the total number of molecules, once each linear molecule has two end:

$$DP = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{1+r}{2r(1-p) + 1-r}$$

Or at complete conversion ( $p = 1$ ) :  $DP = (1 + r) / (1 - r)$

■ *Scheme 3.* Dependence of the DP on the molar rate of  $a_2/b_2$  (here A/B) monomers, as defined by P. Flory.<sup>[2]</sup>

to their low  $T_g$  (−50 to −60 °C depending on the DP), telechelic polyesters can serve as soft segments in thermoplastic elastomers such as elastic polyurethanes. In this application, aliphatic polyesters compete with telechelic poly(ether diol)s.

At this point it should be mentioned that P. Flory has elaborated mathematical formulas correlating the excess of one monomer with the DP (Scheme 3).<sup>[2]</sup> However, Flory did not consider the role of cyclization in his theory of step-growth polymerization. The excess of one monomer strongly reduces the efficiency of cyclization, because all the oligomers and polymers having two identical end groups cannot cyclize. The predominance of chains having two identical end groups decreases when the stoichiometry approaches unity (see below), and Flory's equation approaches the reality mainly for non-stoichiometric polycondensation with an excess >10%.

### 2.1.2 Non-Stoichiometric Polycondensations in Solution

Several commercial polycondensates are technically produced in solution, for example, polyaramides, polyimides, poly(ether sulfone)s and poly(ether ketone)s. These polymers are normally produced on the basis of stoichiometric monomer mixtures, and the molar masses are controlled by the addition of monofunctional chain terminators or by time and temperature (i.e., by incomplete

conversion). However, non-stoichiometric polycondensations may be of interest for the preparation of telechelic oligomers and polymers. Due to high  $T_g$ s and good solubility in various organic solvents, telechelic poly(ether sulfone)s have been prepared by several research groups.<sup>[20–22]</sup> Usually the diphenol was used in excess to obtain chains having two phenolic OH end groups. Various block-copolymers were prepared from these telechelics, and their mechanical and physical properties were studied. Further telechelic oligomers based on polycondensations with an excess of a diphenol have been described in the literature<sup>[20,21]</sup> (an exhaustive citation of all papers dealing with telechelic oligomers having two phenolic end groups is not intended).

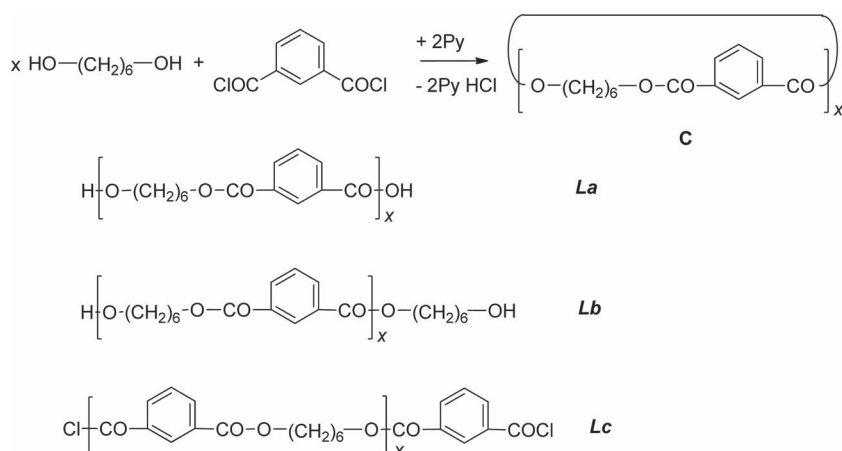
For  $a_2 + b_2$  polycondensations in solution with the purpose of preparing high molar mass polymers, three different experimental procedures may be considered (in contrast to **a-b** monomers). These three procedures are here exemplarily discussed for pyridine-promoted polycondensations of 1,6-hexanediol and isophthaloyl chloride (IPCl) (Scheme 4).

**Method A:** 1,6-hexanediol and IPCL are mixed in solution and pyridine is (slowly) added.

**Method B:** 1,6 hexanediol and pyridine are mixed in solution and a solution of IPCL is slowly added.

**Method C:** A solution of 1,6-hexanediol and pyridine is slowly added to a solution of IPCL.





**Scheme 4.** Reaction products resulting from polycondensation of 1,6-hexanediol and IPCL.

As for any other **a**<sub>2</sub> + **b**<sub>2</sub> polycondensation, four reaction products will be formed (Scheme 4)

These are cycles (labelled **C**), linear chains having one “a” and one “b” end group (labelled **La**), chains having two nucleophilic (OH) end groups (labelled **Lb**) and chains having two electrophilic (CO-Cl) end groups (labelled **Lc**). This system of labelling reaction products will be used throughout this work in agreement with previous publications of the first author.

When a polycondensation is conducted according to method **A**, and when it takes an ideal course, the molar ratio of **La/Lb/Lc** will be 2/1/1 regardless of the conversion. Only **La** chains can cyclize, but reactions of **Lb** with **Lc** chains yield **La** chains, and thus, the fraction of cycles increases with higher conversions until all reaction products are cycles at 100% conversion. In the case of method **B**, **Lb** chains which cannot cyclize are the predominant reaction products up to high conversions and the competition of cyclization is reduced. However, when all IPCL is added to the reaction mixture, cyclization becomes the main reaction, because the fraction of **La** chains (relative to **Lb** and **Lc**) increases, whereas its absolute molar fraction is low and further decreases with higher conversions according to the law of self-dilution.<sup>[23]</sup> The low concentration of **La** favors cyclization due to the Ruggli-Ziegler Dilution Principle.<sup>[24]</sup> In other words, method **B** also yields cycles at 100% conversion, but their average molar mass is higher than that of the cycles obtained via method **A**. Method **C** is the mirror image of method **B**. Initially, the formation of **Lc** chains is favored and the influence of cyclization is suppressed, but with increasing conversion and finally perfect stoichiometry, cyclization again becomes the main reaction.

To the best of our knowledge, a systematic study of the three different procedures and their consequences for chain growth has never been published. However, a few experiments conducted for this work and compiled

in Table 1 suggest that the aforementioned considerations are correct. All polycondensations of 1,6-hexanediol and IPCL conducted via method **B** gave higher molar masses than those performed via method **A**. The degree to which methods **B** and **C** contribute to chain growth at the expense of cyclization depends on the rate of chain growth versus the rate of monomer addition. As discussed below, interfacial polycondensations may be particularly well suited to profit from this scenario.

### 2.1.3. Interfacial Polycondensations

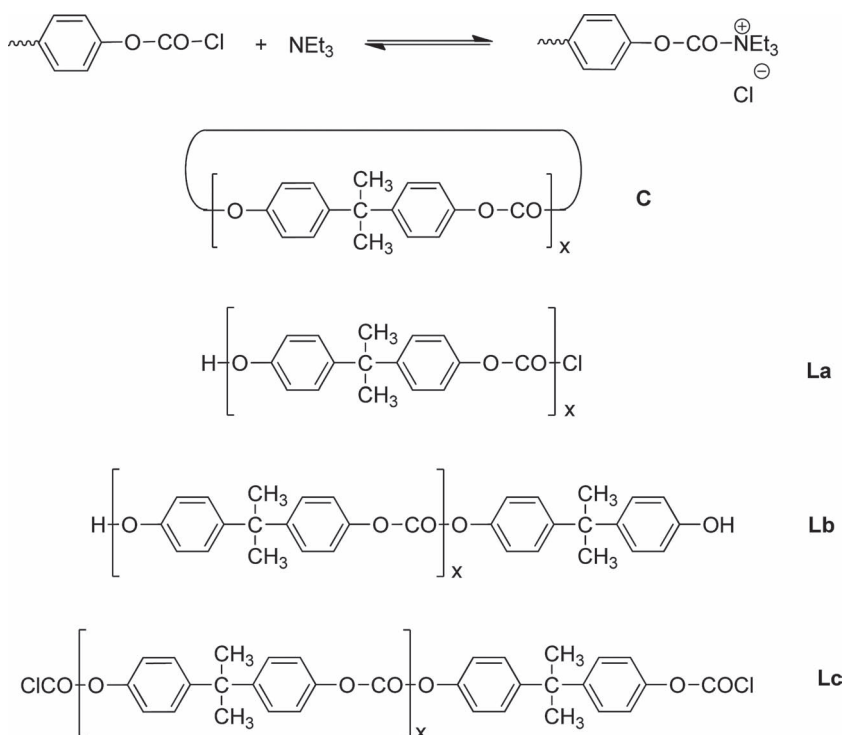
The synthetic strategy of interfacial polycondensations was formulated for the first time for the preparation of polyamides by E. Magat and D. R. Strachan in a US patent in 1955.<sup>[25]</sup> In the years 1959–1965, P. W. Morgan and co-workers elaborated a broad and detailed study of interfacial polycondensations for various polymers.<sup>[26–28]</sup> This strategy has found broad applications for research purposes, because relatively high molar masses can be obtained without perfect stoichiometry. However, for the technical production of polymers it has two disadvantages. First, dry organic solvents are needed when reactive monomers such as dicarboxylic acid chlorides or phosgene are used. Second, large amounts of salt solutions are formed as by-products. Nonetheless, the production of polycarbonates by interfacial phosgenation has proven to be a viable technical process for more than 50 years.<sup>[29,30]</sup>

The commercial polycarbonates mainly or exclusively consist of bisphenol-A and usually possess usually  $\bar{M}_n$ s below 30 000 Da. When polycarbonates are processed by extrusion (e.g., for the production of safety glass) relatively high  $\bar{M}_n$ s are used. For injection molding, low melt viscosities are advantageous, and the  $\bar{M}_n$ s of polycarbonates used for compact discs usually fall in the range 11 000–13 000 Da. Therefore the chemical industry

**Table 1.** Polycondensation of 1,6-hexanediol and isophthaloyl chloride (IPCL).

Exp. No.	Method <sup>a)</sup>	Excess of IPCL (mol%)	Yield (%)	$\bar{M}_n$ (Da) <sup>b)</sup>	PD <sup>b)</sup>
1	A	0	89.0	5000	2.75
2	A	2	89.5	5200	3.30
3	B	0	84.0	5500	2.40
4	B	2	88.0	6200	3.20

<sup>a)</sup>In dichloromethane at 20–25 °C; <sup>b)</sup>SEC measurements in THF calibrated with polystyrene.



**Scheme 5.** Activation of chloroformate groups and reaction intermediates in the phosgenation of bisphenol A.

did not have much interest in exploring reaction conditions yielding maximum  $\overline{M}_n$ s.

Fifty years after the invention of aromatic polycarbonates, the first author of this article launched a detailed study on the phosgenation of bisphenol A and bisphenol M. Dichloromethane and aqueous sodium hydroxide solutions served as reaction media (in analogy to the technical process), and triethylamine or quarternary phosphonium salts were used as phase transfer (PT) catalysts. Triethylamine is the standard catalyst for technical phosgenation, and it has been known for a long time that it plays a dual role in this process. First, it forms a salt with the phenolic OH groups and acts as a PT catalyst. Second, it forms a complex with phosgene and chloroformate groups (Scheme 5). This complex activates the chloroformate groups and accelerates chain growth and cyclization, but also favors hydrolysis. In contrast, quarternary phosphonium or ammonium salts exclusively act as PT catalysts. This difference needs to be noted, because triethylamine and the other PT catalysts showed opposite trends in otherwise identical phosgenation experiments (Table 2).<sup>[31,32]</sup> Triethylamine gave the highest molar masses at low catalyst concentration, whereas tetrabutyl ammonium chloride yielded the highest molar masses at high catalyst concentrations. SEC measurements based on triple detection gave  $\overline{M}_n$  values in the range 300–400 kDa with  $\overline{M}_w$ s above 1000 kDa. To the best of our knowledge, these

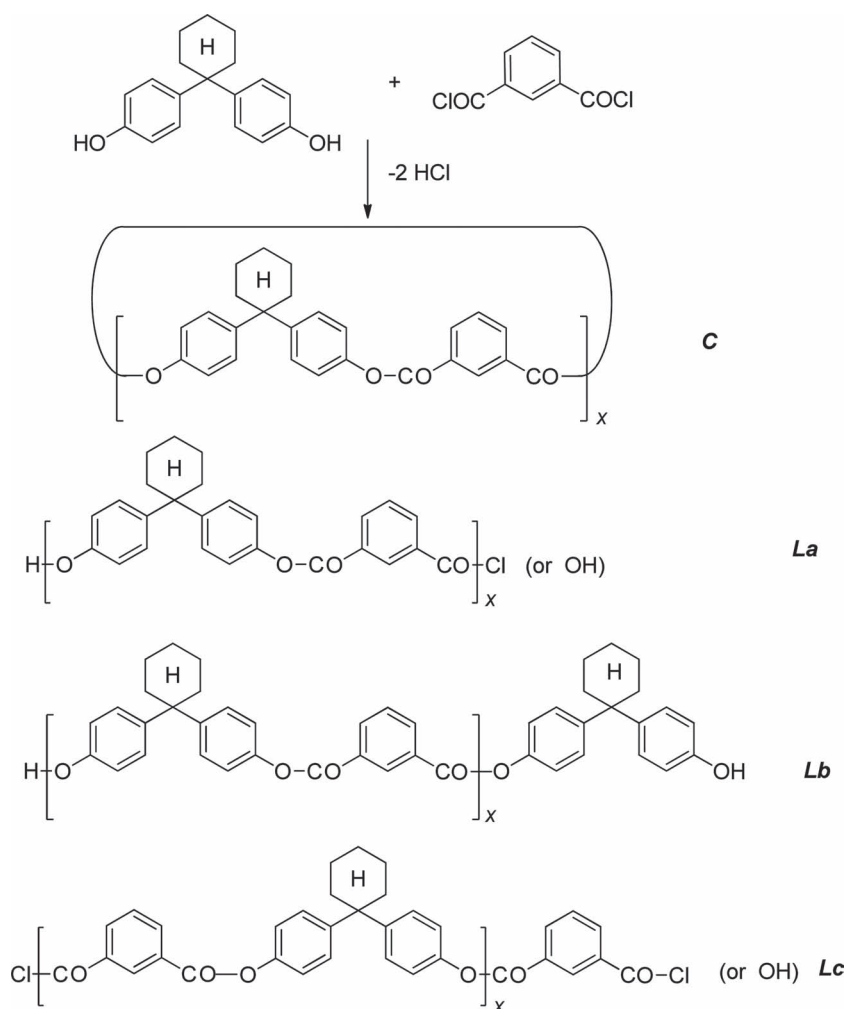
are the highest reliably measured molar masses of polycondensates reported so far (high  $\overline{M}_n$ s reported for membrane osmosis measurements are meaningless, because that method is intrinsically unsuitable for the characterization of polycondensates). The MALDI-TOF mass spectra of the best polycarbonate samples exclusively displayed peaks of cycles indicating that the reaction conditions were close to the optimum. In the case of samples fractionated by SEC, cycles up to 55 000 Da were detectable<sup>[32]</sup> and larger cycles were certainly present, but the limitation of the MALDI method did not allow for their detection. In summary, it may be concluded that an interfacial phosgenation of diphenols is a pseudo-ideal polycondensation, because the only significant side reaction, the hydrolysis of chloroformate groups, can be compensated for by an excess of (di)phosgene.

Finally several polycondensations of bisphenol A and diphosgene were conducted in a homogeneous phase (dichloromethane + dioxane) with pyridine as a catalyst and HCl acceptor. The amount of diphosgene was varied to compensate for decomposition and other side reactions. The best result was a  $\overline{M}_n$  of 15 000 Da. The MALDI-TOF mass spectrum displayed an almost exclusive formation of cycles indicating that stoichiometry and reaction conditions were close to the optimum. These results mean that the maximum  $\overline{M}_n$ s which can

**Table 2.** Influence of catalyst concentration on the molecular weight in interfacial phosgenations of bisphenol A. Data taken from ref. [32].

Exp. No.	Catalyst	Cat./Bisphenol A	Inh. Visc. (dL g <sup>-1</sup> ) <sup>a)</sup>
1	Triethylamine	2/20	7.71
2	Triethylamine	4/20	3.42
3	Triethylamine	8/20	0.82
4	Triethylamine	12/20	0.32
5	TEBA-Cl <sup>b)</sup>	1/20	0.18
6	TEBA-Cl <sup>b)</sup>	2/20	0.89
7	TEBA-Cl <sup>b)</sup>	4/20	3.29
8	TEBA-Cl <sup>b)</sup>	8/20	6.35
9	TEBA-Cl <sup>b)</sup>	12/20	6.80 <sup>c)</sup>

<sup>a)</sup> Measured at 20 °C with  $c = 2 \text{ g L}^{-1}$  in dichloromethane; <sup>b)</sup> Tetrabutyl ammonium chloride; <sup>c)</sup>  $\overline{M}_n = 295 \text{ kDa}$ ,  $\overline{M}_w = 1050 \text{ kDa}$  (by SEC).



■ Scheme 6. Polycondensation of bisphenol C and isophthaloyl chloride.

be achieved by interfacial polycondensation are at least a factor of 20 higher than those obtainable in a dry homogeneous reaction medium.<sup>[33,34]</sup> This conspicuous result can be explained in the following way. The diphenol anion is gradually transported into the organic phase where it is confronted with an enormous excess of (di)phosgene and oligomers and polymers having two chloroformate end groups (Lc chains in Scheme 5). Therefore, the intermediately formed La chains, the only species which can cyclize, will rapidly react with (di)phosgene or Lc chains yielding new Lc chains. Therefore the chance for cyclization is much lower than in homogeneous polycondensations where the La chains are the predominant intermediates. Yet, close to the end of the polycondensation, when all the (di)phosgene and part of the chloroformate groups are consumed by hydrolysis and condensation steps, the La chain will prevail and cyclize, so that finally most of the reaction products are cyclic polycarbonates, but with a higher average DP than in the case of an analogous polycondensation in the homogeneous phase.

If this interpretation is correct, the trend that interfacial polycondensations yield higher molar masses than the corresponding polycondensations under homogeneous conditions should also be observable for other monomer combinations. However this aspect has never been investigated in previous studies of interfacial polycondensations, just as the role of cyclization in step-growth polymerization has largely been ignored due to the influence of Flory's theory.

At this point it should be noted that, for several reasons, polycondensations of diamines and dicarboxylic acid dichlorides are not suitable for such studies. Firstly, all polyamides forming H-bonds are insoluble in the inert solvents needed for interfacial polycondensations. Secondly, aromatic diamines are not nucleophilic enough to compete with hydrolysis of the acid chloride groups. Thirdly, aliphatic diamines are too basic for clean polycondensations in a homogeneous phase. Therefore, polycondensations of 1,1-bis(4-hydroxyphenyl)cyclohexane (bisphenol C) with isophthaloyl chloride (Scheme 6) were studied in the present work (the synthesis of this polyester was known before).<sup>[28]</sup> Bisphenol A was replaced with bisphenol C, because it was found that the polyisophthalate of bisphenol A was neither completely soluble in

dichloromethane nor in chloroform. The experiments compiled in Table 3 evidence that, in analogy to the phosgenation of bisphenol A, an increasing amount of PT-catalyst favored higher molar masses in the interfacial polycondensations (Nos. 1–4 in Table 3). Also in analogy with the interfacial polycondensation of bisphenol-A, bimodal molecular weight distributions were observed (Figure 1 and 2, curves A). When the low molar mass maxima of the elution curves were separated by SEC and analyzed by MALDI-TOF mass spectrometry, cyclics were almost exclusively detected (Figure 3).

The polycondensations in homogeneous solutions (No. 7–10) were performed with two different amine catalysts and with slight variation of the stoichiometry to come close to the optimum conditions. In agreement with previous polyester syntheses, the higher molar masses were achieved with a slight excess of isophthaloyl chloride regardless of the tertiary amine. In the case of bisphenol C, the results achieved with pyridine were worse than those obtained with triethyl amine in contrast

■ Table 3. Polycondensations of bisphenol C with isophthaloyl chloride.

Exp. No.	Method	Catalyst	Cat/IPCl	Excess of IPCl (mol%)	Yield (%)	$\overline{M}_n$ (Da) <sup>a)</sup>	PD <sup>a)</sup>
1	Interfacial Pol.	Triethylamine	0.2/100	0	82.0	7000	2.8
2	Interfacial Pol.	Triethylamine	1/100	0	85.5	14 000	3.5
3	Interfacial Pol.	Ph <sub>4</sub> PCL	1/100	0	74.0	170 000	13.0
4	Interfacial Pol.	Ph <sub>4</sub> PCL	2/100	0	73.0	155 000	18.0
5	Interfacial Pol.	Ph <sub>4</sub> PCL	4/100	0	72.0	170 000	18.5
6	Interfacial Pol.	Ph <sub>4</sub> PCL	8/100	0	72.5	175 000	19.5
7	Homogen Pol.	Pyridine	4/1	0	98.5	13 000	2.8
8	Homogen Pol.	Pyridine	4/1	1	99.0	15 000	3.0
9	Homogen Pol.	Triethylamine	4/1	0	99.5	37 000	3.7
10	Homogen Pol.	Triethylamine	4/1	1	99.5	42 000	3.7

<sup>a)</sup>SEC measurements in chloroform at 30 °C calibrated with polystyrene.

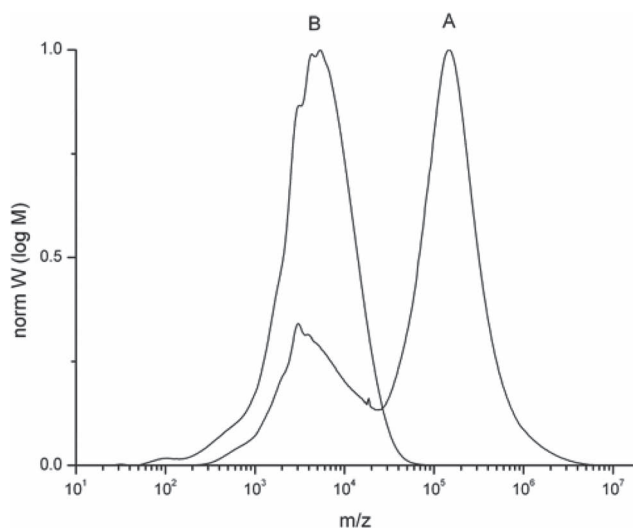


Figure 1. SEC elution curves of poly(bisphenol C isophthalate) s. (A) PT-catalyzed interfacial polycondensation No. 3, Table 3. (B) Pyridine-catalyzed polycondensation in homogeneous solution No. 8, Table 3.

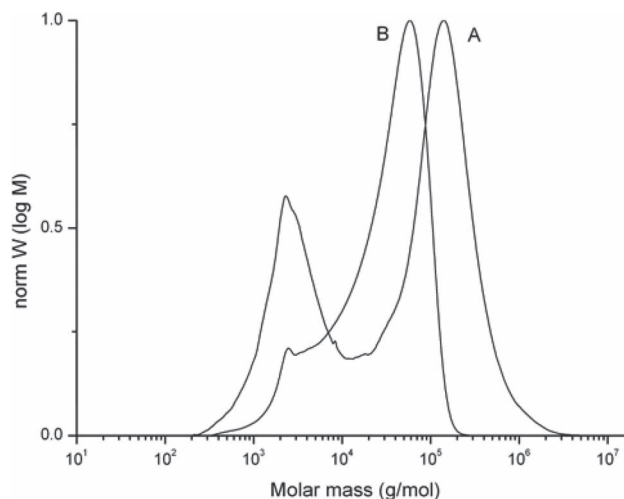


Figure 2. SEC elution curves of poly(bisphenol C isophthalate): (A) PT-catalyzed interfacial polycondensation, No. 5, Table 3. (B) Triethylamine-catalyzed polycondensation in homogeneous solution No. 9, Table 3.

to the above-mentioned polycondensations of 1,6-hexanediol. Monomodal molecular weight distributions were found (Figure 1, curve A) and the MALDI TOF mass spectra revealed incomplete conversions and side reactions. For the triethylamine catalyzed samples (No. 9, 10, Table 3) the MALDI-TOF mass spectra revealed almost complete conversion with formation of cyclics, so that the mass spectra were nearly identical with that of Figure 3. Surprisingly, the SEC elution curves of the triethylamine catalyzed samples displayed a slight tendency in the direction of a bimodal distribution (Figure 2, curve B).

In other words, the correlation between synthetic method and molar masses agreed with the trends observed for syntheses of polycarbonates. Hence, the explanation is the same. The **Ic** chains (Scheme 6) are the

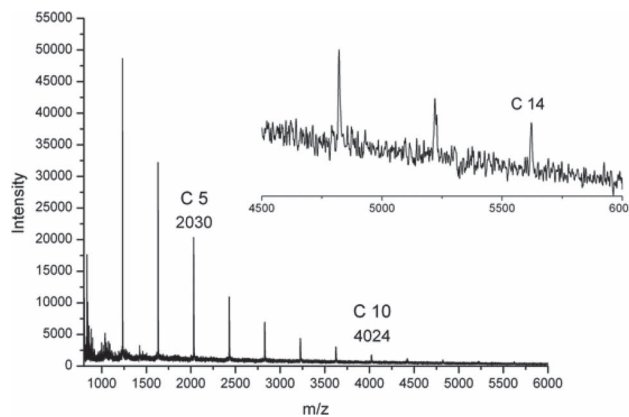
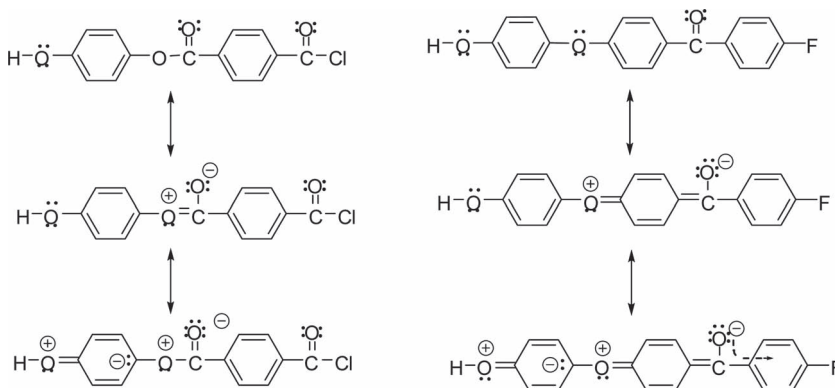


Figure 3. MALDI-TOF mass spectrum of the low molar mass fraction of poly(bisphenol C isophthalate), No. 5, Table 3.



prevailing species up to high conversions, and thus cyclization will mainly occur at high conversions, when relatively long chains have already been formed. The SEC measurements also revealed another analogy. The SEC elution curves of the interfacial polyesters were bimodal with a maximum in the low molar mass range and a considerably higher maximum in the high molar mass range (Figure 1, curve A). When the low molar mass fraction was isolated by SEC, MALDI-TOF mass spectra revealed that this fraction exclusively consisted of cycles (Figure 3). Similar elution curves were found for polycarbonates prepared by interfacial polycondensation, whereas the polycarbonates and polyesters prepared in a homogeneous phase gave a normal monomodal elution curve (Figure 1, curve B). The lower molar masses of the polyesters relative to those of the polycarbonates are mainly a consequence of the fact that hydrolysis of acid chloride groups generates dead end groups. Therefore it is particularly remarkable that, under homogeneous conditions which reduce the risk of hydrolysis, the molar masses are lower. The MALDI-TOF mass spectra of the polyesters prepared in the homogeneous phase (No. 7–10, Table 3), which almost exclusively display peaks of cycles, prove that not low conversions but efficient cyclization was the reason for the limitation of the chain growth. Therefore, these results clearly demonstrate that the course of interfacial polycondensations can only be rationalized when the role of cyclization is taken into account.

A significant influence of a biphasic reaction mixture on the competition between chain growth and cyclization is not limited to interfacial polycondensation involving two liquid phases. Reactions between a dissolved monomer and a solid reaction partner may also obey the trends discussed above. A typical example is the polycondensation of dichloro methyl phenyl silane mediated by metallic sodium in toluene under ultrasonic irradiation.<sup>[35]</sup> Since the resulting oligo- and polysilanes can delocalize radicals and electric charges along their conjugated backbone, the Si–Cl end groups are more reactive towards sodium than the Si–Cl groups of the monomers. At first a radical anion is formed which, after elimination of a Cl anion, yields a sodium silicide end group. The silicide anion reacts fast with Si–Cl groups of monomers, because they are more electrophilic than the Si–Cl groups of oligomers and polymers due to the lack of conjugation. Hence, in the early stages of polycondensation the reaction mixture mainly contains polysilane chains having two Si–Cl end groups, which cannot cyclize but continue the chain growth. Consequently, long polysilane chains are formed at low



■ Scheme 7. Mesomeric formulas of ethers and esters formed from hydroquinone.

conversions, but more and more cycles are formed at higher conversions.

## 2.2. Type II Polycondensations

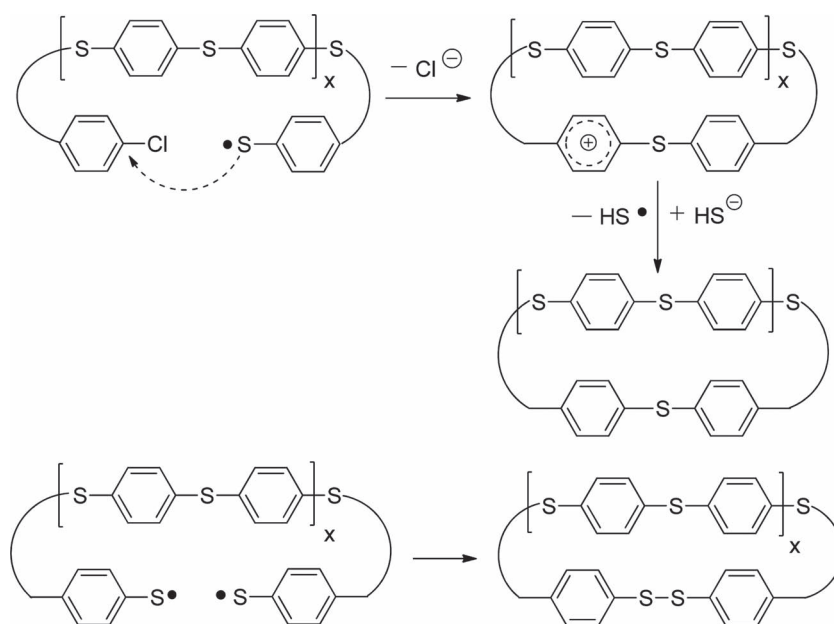
This group of polycondensations is characterized by relatively rapid reactions between  $a_2$  and  $b_2$  monomers. In other words, the reaction between  $a_2$  and  $b_2$  monomers results in a (slight) deactivation of the “a” and “b” end groups of the dimer and longer chains. Examples of such a kinetic scenario are rare and mainly concern polycondensations of hydroquinone or catechols with aromatic reaction partners, such as 4,4-dichlorodiphenylsulfone, 4,4'-difluorobenzoquinone (Scheme 7, right) or terephthaloyl chloride (Scheme 7, left). The mesomeric formulas presented in Scheme 7 illustrate how the delocalization of electron pairs reduces the reactivity of the end groups of the dimers. When long diphenols with interrupted conjugation are used, such as bisphenol A, the reactivity of the OH groups is, of course, not affected by the formation of ester or ether groups, and polycondensations of such diphenols do not belong to type II. In the case of true type II polycondensations, an excess of one monomer has the only consequence that telechelic oligomers will be formed, quite analogous to Type I polycondensation, and thus, a further discussion of Type II polycondensations is not needed.

## 2.3. Type III Polycondensations

The apparently oldest successful non-stoichiometric polycondensation of Type III is a synthesis of poly(phenylene sulfide), PPS, patented by J. Edmonds and H. Hill in 1967.<sup>[36]</sup> Low molar mass PPS was first mentioned in 1878 as an undesired by-product, when Friedel and Crafts studied  $AlCl_3$  catalyzed reactions of benzene with elemental sulfur.<sup>[37]</sup> A more detailed study of this reaction was published by P. Genvress about ten years later.<sup>[38,39]</sup> It took fifty more years until a more attractive laboratory method was

reported by McCallum.<sup>[40]</sup> He described the polycondensation of 1,4-dichlorobenzene with sulfur and potassium carbonate in the melt. Unfortunately, this approach involves branching and crosslinking reactions, the extent of which increases with time and temperature. R. Lenz and other co-workers of Dow Chemical Company attempted to eliminate or reduce the problems associated with the A. McCallum reaction<sup>[41–43]</sup> but a satisfactory procedure allowing for a technical production of PPS was not found. In contrast, the polycondensation of 1,4-dichlorobenzene with sodium sulfide in a polar solvent such as N-methylpyrrolidone, as described by J. Edmonds and H. Hill, yields perfectly linear PPs.<sup>[36]</sup> The relatively low molar masses obtained by the original procedure can be raised to values of around 35 000 Da by the addition of metal carboxylates as catalysts.<sup>[44]</sup> Based on this process, PPS was commercialized by Phillips Petroleum under the trade mark Ryton. Several variations of the synthetic procedure and of the chemical structure were later reported by other authors.<sup>[45]</sup>

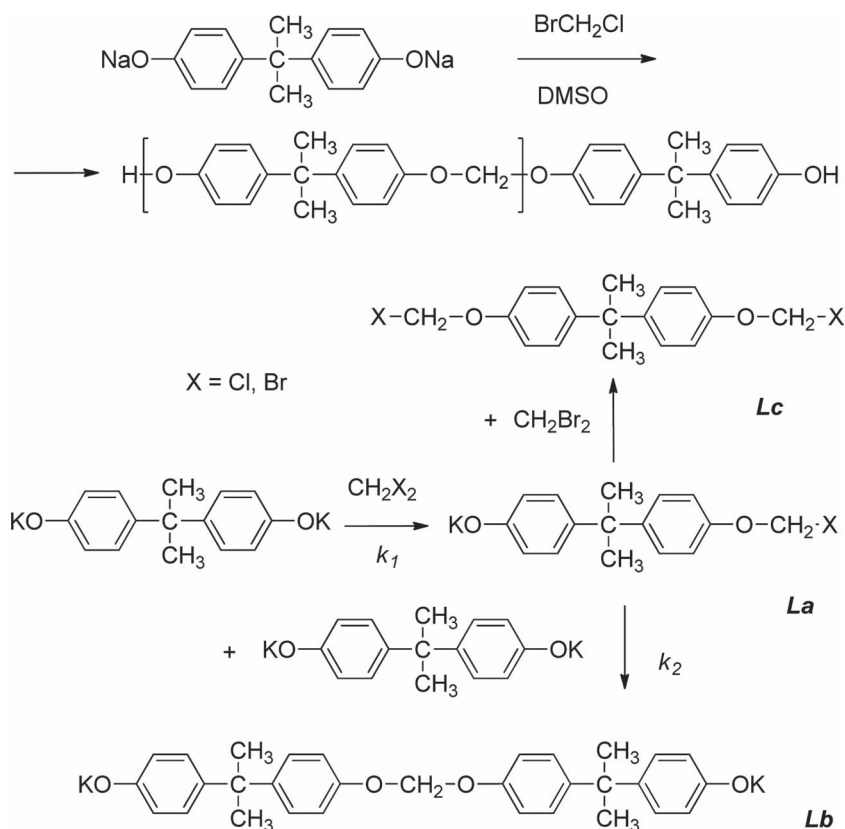
Typical for the Edmonds–Hill approach is the finding that an excess of sodium sulfide accelerates the chain growth and enhances the molar mass. Both effects are also characteristic for all Type III polycondensations discussed below. However, in the case of PPS, an excess of sodium sulfide has the additional effect that more than the stoichiometric amount of sulfur is incorporated in the form of disulfide groups. Sergeev and Nedelkin proposed<sup>[46,47]</sup> a simple nucleophilic substitution in analogy to the mechanism proposed by R. Lenz et al. for polycondensations of 4-chloro- (or bromo-)thiophenol,<sup>[43]</sup> but such a mechanism cannot explain the formation of disulfide groups. In a detailed mechanistic study including various model reactions, Koch and Heitz also observed that the reactivity of the C–X bonds increased in the order Cl < Br < I.<sup>[48,49]</sup> This order is in contradiction to the pattern of the classical nucleophilic substitution at aromatic C–X bonds which is: F >> Cl > Br > I. Yet, the order of reactivity found by Koch and Heitz is known from radical nucleophilic substitution (S<sub>NR</sub>) first described by Bunnet.<sup>[50]</sup> Those authors also found using SEC measurements that relatively high molar mass oligomers are formed at conversions < 50%, in contradiction to Carothers classical theory of polycondensation. Koch and Heitz postulated the radical cationic mechanism and called this reaction pathway a “reactive intermediate mechanism”. They assumed that the oligomeric radical



**Scheme 8.** Potential formation of cycles in the synthesis of PPS from 1,4-dichlorobenzene and Na<sub>2</sub>S.

cations resulting from the attack of an activated monomer onto an oligomeric chain end are better stabilized by delocalization and thus react preferentially with the monomer. A mathematical treatment of this PPS synthesis was published by Rajan et al.<sup>[51,52]</sup> Second order kinetics were found for the first 50% of conversion followed by a 40 times faster chain growth. However, the mechanism of Koch and Heitz does not answer the following questions. Firstly, how is the H–S radical formed, which initiates the entire process? Secondly, why do metal carboxylates catalyze these polycondensations? Thirdly, are cycles formed, and how is their formation correlated with the excess of sodium sulfide? The mechanism of Koch and Heitz allows, in principle, the formation of cyclic sulfides and disulfides (Scheme 8) which will, in turn, reduce the efficiency of the chain growth. Since analytical methods allowing for the detection of cyclics in the reaction mixture did not exist at that time, it is not surprising that a discussion of cyclization reactions was not included in the mechanistic discussions. In summary, the reaction mechanism of the synthetic method patented by Edmonds and Hill is still far from properly understood.

Another class of non-stoichiometric polycondensations was elaborated by Hay et al.<sup>[53–55]</sup> at General Electric around 1983, namely the synthesis of polyformals from diphenols and dibromo- or dichloromethane (Scheme 9). Twenty years before that, Barclay<sup>[56]</sup> had prepared telechelic, low molar mass polyformals from stoichiometric amounts of bromochloromethane and the potassium salt of bisphenol A in hot DMSO (Scheme 9). How-



**Scheme 9.** Potential reaction steps and products in stoichiometric polycondensations of bisphenol A salts with dihalomethanes.

ever, that work did not provide any hint to the advantageous use of non-stoichiometric monomer mixtures. Further interesting results were contributed by organic chemists. A. Kellop et al. observed that bis-(4-tert-butyl phenoxy)methane was formed as the main product when 4-tert-butyl phenol was alkylated with benzylchloride in dichloromethane under phase-transfer conditions.<sup>[57]</sup> Furthermore, Dehmlow and Schmidt reported that high yields of bis(phenoxy)methane could be obtained when phenol and solid KOH were stirred in dichloromethane at 20–22 °C.<sup>[58]</sup> These results indicated that the intermediately formed phenoxychloromethane is far more reactive than the monomer dichloromethane which was used as the reaction medium in large excess.

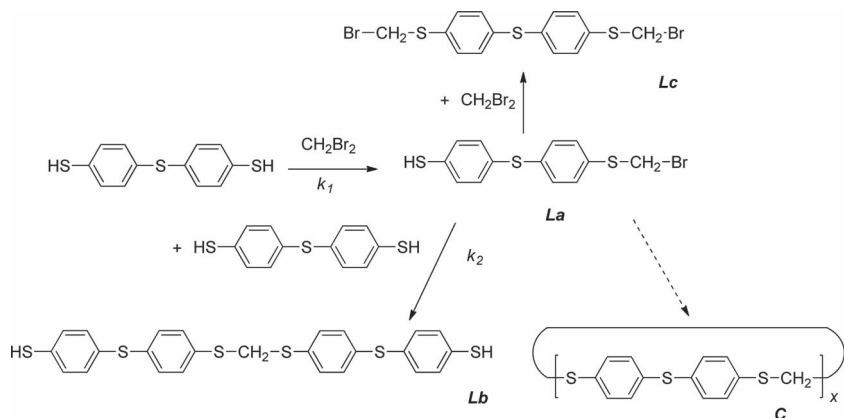
On the basis of these results, A. S. Hay et al. explored the polycondensation of bisphenol A with KOH in dichloromethane using a tetraalkyl ammonium chloride as PT-catalyst. They observed that a thick, pasty mass of the dipotassium salt of bisphenol A was first obtained which reacted slowly with dichloromethane. The expected polyformal was isolated after 18 h in a yield of 49%. After raising the temperature from 25 to 35 °C, the yield increased to 70% and the inherent viscosity of the isolated polyformal doubled. In a mixture of dichloromethane and chlorobenzene, a reaction temperature of 75 °C was

reached, whereby the yield rose to 93% within 4 h. A similar yield and viscosity was obtained in a dichloromethane-*N*-methylpyrrolidone mixture in a much shorter time (1 h). The use of NaOH again gave similar results.

Those authors also observed that the amorphous polyformal contained a small fraction of crystalline material which was isolated and identified as cyclic dimer and trimer. With these cycles in hand, the peaks of oligomers in the high resolution SEC curves were calibrated and cyclic oligomers up to a DP of 25 were detected in the reaction mixtures. Depending on the reaction conditions, the fraction of cycles reached an extent of 66%. Higher temperatures, higher concentrations of the PT-catalyst and the use of a polar solvent (e.g., *N*-methyl pyrrolidone) favored higher yields, higher molar masses and shorter reaction times. Finally, those authors found that the speed of stirring and mixing had a significant influence on the result. Adding an excess of dibromomethane to a preformed suspension of the potassium salt of bisphenol A at 80 °C in *N*-methylpyrrolidone using a

high-speed stirrer gave the highest molar masses and polyformals free of cyclic oligomers (but not necessarily free of cyclic polymers).  $\bar{M}_n$  values up to 250 000 Da were reported ( $\bar{M}_w = 333800$  Da).

A. Hay et al. forwarded the following mechanistic explanation. When only small amounts of bisphenol A salts slowly dissolve in a non-polar reaction medium, the slowly formed **La** species (monomer and oligomers, Scheme 9) will have a relatively high concentration compared to **Lb** and **Lc** chains which cannot cyclize. The formation of cycles is then favored because the absolute concentration of **La** chains is low, so that cyclization dominates over the intermolecular condensation of two **La** chains according to the “Ruggli-Ziegler Dilution Principle”. All parameters favoring a rapid dissolution of bisphenol A salts in the reaction medium accelerate the transformation of **La** chains into **Lb** chains, because the reactivity of the  $\text{OCH}_2\text{Cl}$  (or Br) groups is far higher than that of  $\text{CH}_2\text{X}_2$  ( $k_2 \gg k_1$  in Scheme 9). In other words, those authors attributed the success of a rapid polycondensation yielding high molar masses mainly to the suppression of cyclization. Therefore, the results of Hay et al. demonstrate that the course of Type III non-stoichiometric polycondensations requires the role of cyclization to be considered to understand it properly.



**Scheme 10.** Reaction steps and products of the polycondensation of dibromomethane with 4,4'-thiobisbenzenethiol.

From a preparative point of view, it is worth mentioning that the Hay group prepared polyformals of more than fifteen different diphenols. Furthermore, copoly(esterformal)s were synthesized starting out from OH-terminated telechelic oligoethers, which were obtained by polycondensation of the bisphenol A dipotassium salt and 1,4-bis(chloromethyl)benzene. This oligomerization is a normal Type I polycondensation, because the reactivities of the end groups of the oligomers are identical with those of the monomers. Furthermore, fluorine containing polyformals were prepared by a Japanese research group,<sup>[59]</sup> and the kinetic phenomena reported by the Hay group were again observed, but molecular weight measurements were not performed.

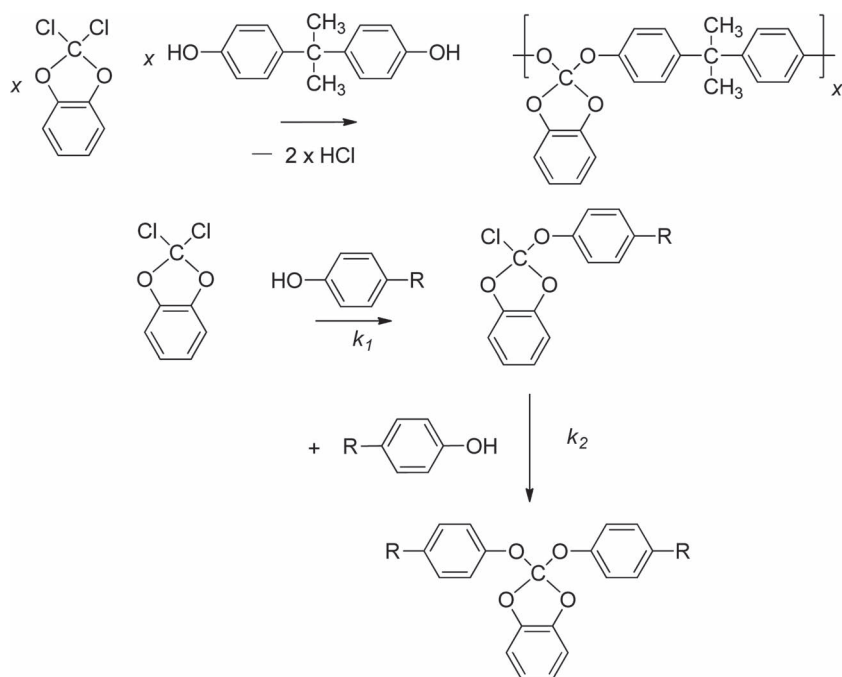
A similar non-stoichiometric polycondensation was also reported by Ueda and co-workers.<sup>[60]</sup> They studied the reaction between 1,4-bis(mercapto)diphenylsulfide and dibromomethane (Scheme 10). They again found two stage kinetics (with  $k_2 = 61 \times k_1$ ) and observed that the excess of dibromomethane enhanced the reaction rate and molar mass. However, concrete  $\bar{M}_n$  or  $\bar{M}_w$  measurements were not reported.

In 1999, Endo and co-workers described polycondensations of bisphenol A with 2,2-dichloro-1,3-benzodioxol, a process yielding aromatic poly(ortho-carbonate)s under evolution of gaseous HCl (Scheme 11).<sup>[61]</sup> Two stage kinetics were found, and, from model reactions using 4-alkyl phenols as substitutes of bisphenol A, a  $k_2/k_1$  ratio of 27 was deduced. An excess of the dichloro monomer accelerated the

entire process and gave higher molar masses. Systematic variation of the feed ratio resulted in a maximum  $\bar{M}_n$  of 120 000 Da (polydispersity 2.5) based on polystyrene-calibrated SEC measurements. Although those authors also performed molecular orbital calculations to provide a theoretical background for the reactivities of the reaction partners, they did not discuss the role of cyclization and they did not interpret the reaction pathway on the basis of the reaction intermediates **La**, **Lb**, **Lc** and **C** (Scheme 12). Yet, it is obvious that the influence of an excess of 2,2-dichloro-1,3-benzodioxol is quite similar to that of dichloromethane in

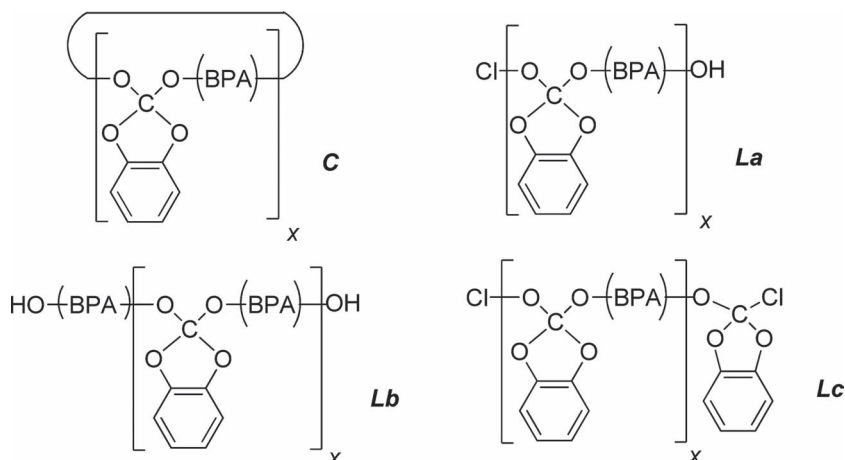
the work of A. Hay et al. An excess of the electrophilic reaction partner reduces the lifetime and concentration of the **La** chains and, thus, suppresses the negative effect of cyclization reactions.

Finally, super acid catalyzed polyalkylation of aromatic monomers need discussion. The hydroxyalkylation and polycondensation of phenols with aldehydes or their substitutes has been known since 1872 from a publication of von Bayer.<sup>[62]</sup> Afterwards, numerous authors contributed papers and patents to this field of work and, in 1907, Baekeland patented a procedure suitable for the technical production of Bakelite based on the polycondensation of phenol and formaldehyde.<sup>[63,64]</sup> Over the last ten years,



**Scheme 11.** Overall reaction and individual reaction steps in the polycondensation of bisphenol-A and 2,2-dichloro-1,3-benzodioxole.





**Scheme 12.** Reaction products of the polycondensation of bisphenol-A and 2,2-dichloro-1,3-benzodioxole.

Zolotukhin et al. have reported several times on trifluoromethane sulfonic acid (triflic acid) catalyzed polycondensations of fluorinated ketones with various aromatic monomers, such as biphenyl, diphenyl ether or 4,4'-diphenoxybenzophenone.<sup>[65–72]</sup> This process may yield high molar mass polymers when catalyzed by triflic acid and when the ketone is used in excess. The mechanistic course of such a polycondensation is exemplarily outlined in Scheme 13. Further examples of poly(alkylene arylene)s prepared in this way are formulated in Scheme 14. The model reaction of anisol with methane sulfonic acid and triflic acid was studied and a clean para substitution was found.

Regardless of which monomer combination was used, it was found that an excess of the ketone dramatically enhanced the molar masses of the polycondensates. For the polymer derived from trifluoroacetone and 4,4'-diphenoxybenzophenone, a maximum  $\bar{M}_n$  of around 250 000 Da was achieved and the inherent viscosities of the other polymers suggested that, in most experiments,  $\bar{M}_n$  values in the range 100 000–200 000 Da were obtained.<sup>[72]</sup> In most cases relatively high polydispersities were also found (up to 4.5), which suggests, together with small broad signals in the  $^1\text{H}$  NMR spectra, that at long reaction times branching reactions occur which involve the ortho positions of the aromatic repeat units. Kinetic measurements were not performed, but from calculations of activation energies it was concluded that the growing steps ( $k_2$  in Scheme 13) are faster than the

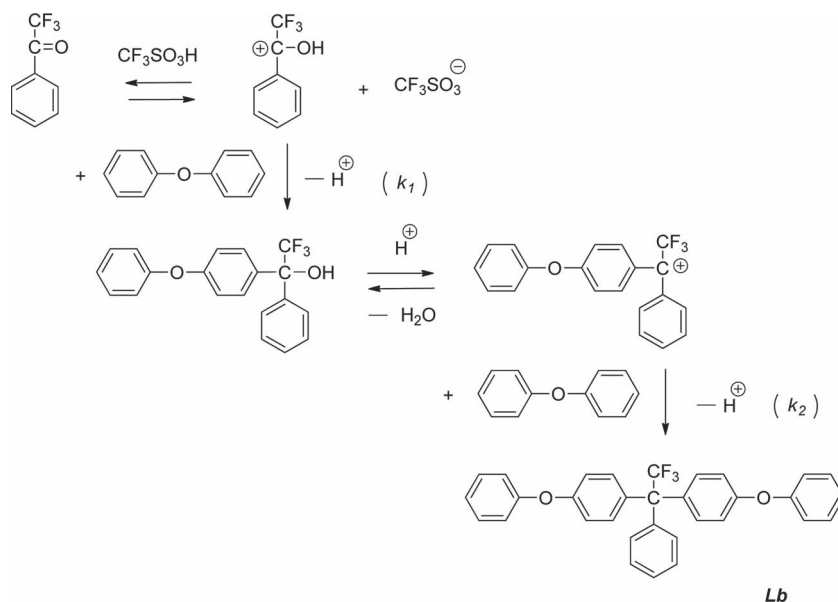
reaction between both monomers ( $k_1$ ). In the MALDI-TOF mass spectra of the low molar mass polymer prepared from equimolar amounts of the trifluoroacetone and 4,4'-diphenoxybenzophenone, cycles were detectable, but the **Lb** chains were largely prevailing. This finding means that the low molar mass was mainly a consequence of low conversion and not so much due to cyclization. Cyclic oligomers were also observed in the mass spectrum of the high molar mass polymer, which means that cyclization was not completely suppressed, even when the excess of the ketone favoured a rapid chain growth. However, a clear cut correlation between reaction conditions and extent of cyclization was

not elaborated, and further studies in this direction are still needed.

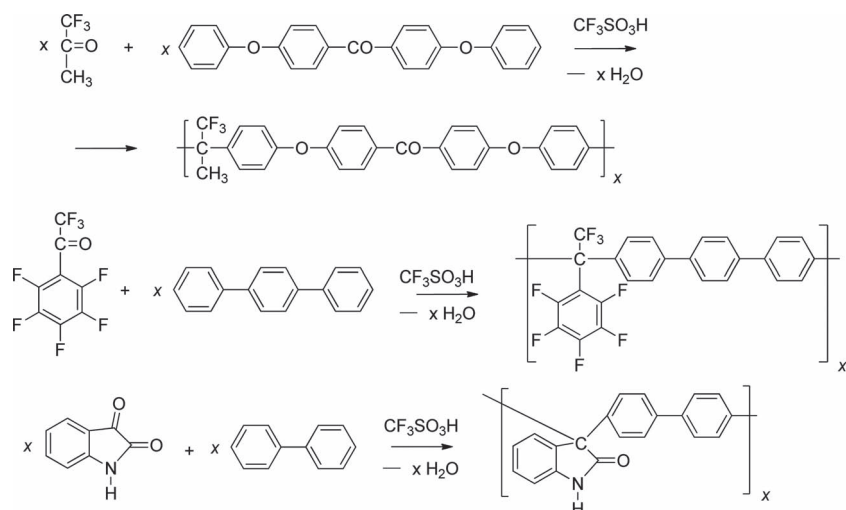
For the sake of completion it should be mentioned that several arylation polycondensations involving two-step kinetics have been published,<sup>[73–79]</sup> but in all cases only stoichiometric feed ratios were used.

#### 2.4. “ $\text{A}_2 + \text{B}_n$ ” Polycondensations

In the case of “ $\text{a}_2 + \text{b}_2$ ” polycondensations, the equimolar feed ratio is necessarily identical to the equifunctional ratio (meaning equal numbers of functional groups). In the case of “ $\text{a}_2 + \text{b}_n$ ” polycondensations, the equimolar and equifunctional monomer ratios are quite different and



**Scheme 13.** Reaction pathway of a superacid catalyzed polycondensation of trifluoroacetone and diphenyl ether.



■ Scheme 14. Examples of the polyalkylation reactions described.<sup>[68,72]</sup>

yield different architectures. Depending on the purpose of a polycondensation, both monomer ratios may be considered to be stoichiometric, but when the terminology of “ $a_2 + b_2$ ” polycondensations is consequently applied, equifunctional feed ratios are non-stoichiometric.

Even when the equifunctional ratio is considered as stoichiometric, three different regimes of non-stoichiometric “ $a_2 + b_n$ ” polycondensations may be defined:

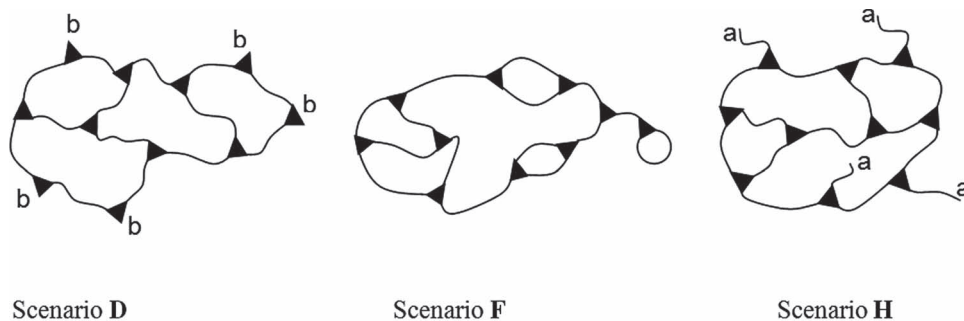
- 1)  $[a_2]/[b_n] < 1.0/1.0$  (equimolar);
- 2) equimolar  $< [a_2]/[b_n] <$  equifunctional (1.5/1.0 for  $b_3$  and 2.0/1.0 for  $b_4$ );
- 3)  $[a_2]/[b_n] >$  equifunctional.

The field of non-stoichiometric “ $a_2 + b_n$ ” polycondensations may be further complicated when two-step kinetics are involved in analogy to the type III polycondensations discussed above. Furthermore, it must be taken into account that the initial monomer concentration (IMC) plays a greater role in the architecture of the reaction products than it does in the case of “ $a_2 + b_2$ ” polycondensations. However, the overriding trend is the same: lower IMCs favor cyclization according to the Ruggli-Ziegler Dilution Principle. From the viewpoint of the resulting

architecture, eight sets of reaction conditions may be defined on the basis of the aforementioned parameters considering conversions  $> 99\%$ , but without considering kinetic details:

- A)  $[a_2]/[b_n] < 1/1$  and moderate or high IMCs (e.g.,  $> 0.2 \text{ mol L}^{-1}$ ) yield more or less branched oligomers and low molar mass polymers almost free of cyclic elements and exclusively “decorated” with “b” groups.
- B) Equimolar stoichiometry and high IMC (e.g.,  $> 0.6 \text{ mol L}^{-1}$ ) yield (hyper)branched polymers mostly containing a cyclic core and only “b” groups at 100% conversion.
- C)  $[a_2]/[b_n] > 1.0/1.0$  and  $< 1.5/1.0$  ( $b_3$ ) or  $< 2.0/1.0$  ( $b_4$ ) and high IMCs yield gels.
- D)  $[a_2]/[b_n] > 1.0/1.0$  and  $< 1.5/1.0$  ( $b_3$ ) or  $< 2.0/1.0$  ( $b_4$ ) and moderate IMCs (e.g.,  $0.01\text{--}0.2 \text{ mol L}^{-1}$ ) may yield soluble multicyclic polymers rich in “b” groups (see Scheme 15).
- E) Equifunctional feed ratios and high IMCs yield gels.
- F) Equifunctional feed ratios and moderate IMCs (e.g.,  $0.01\text{--}0.1 \text{ mol L}^{-1}$ ) yield multicyclic polymers free of functional groups at 100% conversion (see Scheme 15).
- G) Equifunctional feed ratios and low IMCs (e.g.,  $10^{-5} \text{ mol L}^{-1}$ ) yield bicyclic or tricyclic oligomers.
- H)  $[a_2]/[b_n] >$  equifunctional and high IMCs yield gels and multicyclic polymers having “a” groups at molar ratios close to equifunctional or yield branched oligomers at very high  $[a_2]/[b_n]$  ratios (see Scheme 15).

Polycondensations corresponding to the non-stoichiometric scenarios A, C and G have rarely been studied. The oldest examples of “ $a_2 + b_3$ ” polycondensations correspond to scenarios A and B, namely polycondensations of phenol (or anisol) with formaldehyde or its substitutes (e.g.,  $\text{CH}_2\text{Br}_2$ , dimethoxymethane or hexamethylene tetramine). A first short description of such a polycondensation (based on dimethoxymethane) was published by von Bayer in 1872,<sup>[80]</sup> and the first polycondensation of free



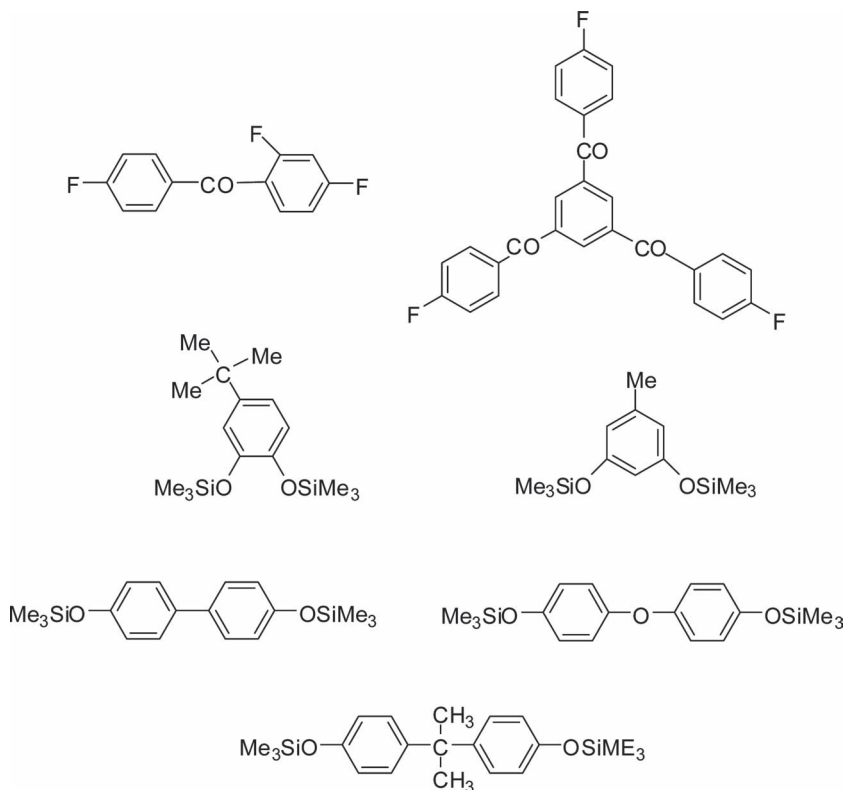
■ Scheme 15. Examples of multicyclic oligomers resulting from “ $a_2 + b_3$ ” polycondensations.



Particularly interesting were polycondensations of silylated THPE with 2,6- and 2,4-difluorobenzonitrile<sup>[93]</sup> or with 2,6- and 2,4-difluorobenzophenone.<sup>[94]</sup> At a THPE concentration of 0.12 mol L<sup>-1</sup>, 2,6-difluorobenzonitrile yielded gels at feed ratios > 1.1/1.0. Yet, at the same IMC, the 2,4- isomer yielded completely soluble polyethers for all feed ratios. Analogous results were obtained from the isomeric difluorobenzophenones (Scheme 16). Conformational analyses by computer modelling revealed that the 2,6-isomers favored extended chain conformations which were disadvantageous for cyclization.<sup>[94]</sup> Non-stoichiometric polycondensations of 2,6-difluoropyridine took the same course as 2,4-difluorobenzonitrile or 2,4-difluorobenzophenone because this monomer favored loop conformations.<sup>[95]</sup> At an IMC of 0.12 mol L<sup>-1</sup> soluble cyclic and multicyclic polyethers were obtained from all feed ratios. An extraordinary MALDI-TOF mass spectrum proved that the formation of perfect multicycles (Scheme 15, scenario F) was not limited to oligomers, but proceeded at least up to masses around 32 000 Da corresponding to a degree of polymerization of 77.

Furthermore, polycondensations of two trifluoroaromatics with various silylated diphenols were reported (Scheme 17).<sup>[96,97]</sup> It was found that the risk of crosslinking increased with greater stiffness of the diphenol and with a wider bond angle between the OH groups. In other words, all structural parameters favoring extended chain conformations were negative for the formation of soluble (multi) cyclic reaction products. Apparently for steric reasons, nearly quantitative conversions were not achieved at the equifunctional feed ratio, regardless of which monomer combination was used. Finally, syntheses of perfect multicyclic polyesters were reported for polycondensations of tri- or tetra(ethylene glycol) with trimesoyl chloride (benzene-1,3,5-tricarbonyl chloride).<sup>[98]</sup> Even at an IMC of 0.4 mol L<sup>-1</sup> gelation did not occur, because the gauche conformations of the oligo(ethylene glycol)s favor cyclization. In contrast *a,o*-alkanediols, which prefer the all-trans conformation, gave gels even at an IMC of 0.04 mol L<sup>-1</sup>. In summary, for all the aforementioned polycondensations the following overriding trends were observed:

- I) The risk of crosslinking (gelation) increases with higher  $[a_2]/[b_3]$  ratios.
- II) Crosslinking is also favored by extended chain conformations of the reaction products.



■ Scheme 17. Monomers used for non-stoichiometric “ $a_2 + b_3$ ” polycondensations.

- III) Cyclization is favoured by dilution.
- IV) Even at an equimolar feed ratio, the reaction products contain considerable amounts of monocyclic species.
- V) Feed ratios above 1.0/1.0 yield more and more complex multicycles, the functionality of which follows the trend illustrated in Scheme 15.

Numerous “ $a_2 + b_4$ ” polycondensations were also studied by several research groups. These include equimolar polycondensations yielding (hyper) branched low molar mass polymers, equifunctional polycondensations at high IMCs yielding gels and equifunctional polycondensations with moderate IMCs yielding soluble, perfect multicycles.

Systematic variations of the stoichiometry were not studied, and thus a more detailed description of these polycondensations is not presented in this work. Polycondensations “ $a_2 + b_4$ ” were also discussed in two recent review articles.<sup>[99,100]</sup>

### 3. Conclusion

Non-stoichiometric polycondensations of “ $a_2 + b_2$ ” monomers have in common that, over a large part of the conversion, the molar ratio of  $a_2$  and  $b_2$  in the liquid phase is far from unity. The primary consequence is a predominance of oligomers and polymers having identical end groups. In a perfectly stoichiometric reaction mixture, chains



having one “a” and one “b” end group prevail and cyclization of these “a-b-chains” competes with chain growth over the whole course of the polycondensation. However, in non-stoichiometric polycondensations, the influence of cyclization is strongly reduced, and extremely high molar mass polycondensates may be obtained, if side reactions are absent.

For most of the conversion many non-stoichiometric polycondensations (above all Type III and interfacial polycondensations) obey the definition of a condensative chain polymerization, CCP (IUPAC terminology). A CCP is characterized by a chain growth kinetic, whereas each growing step involves an elimination step and represents a condensation reaction. In an ideal CCP the chain growth exclusively proceeds by the reaction of monomers with an activated chain end, whereas all other reactions typical for a true polycondensation are absent. In the case of non-stoichiometric polycondensations cyclization and reactions between oligomers or oligomers and polymers may occur. Yet, a significant influence of cyclization is usually limited to high conversions, when the stoichiometry gradually approaches unity, and when the molar concentration of linear chains is very low.<sup>[101]</sup> Combinations of CCP and polycondensation are an attractive approach to the preparation of cyclic polymers. Other examples of combined chain- and step-growth polymerizations have recently been reviewed.<sup>[102]</sup>

In the case of “ $a_2 + b_n$ ” polycondensations, efficient cyclization reactions are desirable because any factor suppressing cyclization favours crosslinking. Non-stoichiometric “ $a_2 + b_n$ ” polycondensations with feed ratios  $> 1.0/1.0$  under conditions avoiding gelation are of great interest, because they yield a new architecture, namely multicyclic polymers. By variation of the stoichiometry, multicycles having pendant “a” or “b” groups and multicycles bare of any functional groups may be prepared (see Scheme 15). Regardless of functional groups, these polymers are promising materials for such applications as thermosets or high temperature adhesives. Yet these and other applications still need to be explored.

## 4. Experimental Part

### 4.1. Materials

Bisphenol A (purity 99.5%), bisphenol-C (1,1-bis(4-hydroxyphenyl)cyclohexane) (purity 99.0%), isophthaloyl chloride (purity 99.0%), 1,6-hexanediol (purity 99.0%) and tetraphenyl phosphonium chloride (TPC) were purchased from Aldrich (Steinheim, Germany) and used as received. Dichloromethane was distilled over  $P_4O_{10}$ , and pyridine was distilled over calcium hydride.

### 4.2. Polymerization Procedure

#### 4.2.1. Polycondensations of 1,6-hexanediol and isophthaloylchloride (IPCl)

4.2.1.1. Method A. 1,6-hexanediol ( $50 \times 10^{-3}$  mol) and IPCl ( $51 \times 10^{-3}$  mol) were dissolved in dichloromethane (100 mL) and a solution of pyridine ( $200 \times 10^{-3}$  mol) in dichloromethane (40 mL) was added dropwise. The reaction mixture was stirred overnight at 22 °C, concentrated to a volume of approx. 90 mL and precipitated into methanol (800 mL).

4.2.1.2. Method B. 1,6-hexanediol ( $50 \times 10^{-3}$  mol) and pyridine ( $200 \times 10^{-3}$  mol) were dissolved in dichloromethane (100 mL) and the solution of IPCl ( $51 \times 10^{-3}$  mol) in dichloromethane was added dropwise over a period of 2 h. The reaction mixture was stirred for 20 h more, and worked up as described above.

#### 4.2.2 Polycondensations of Bisphenol C and IPCl (Table 3)

4.2.2.1. Interfacial Polycondensations (No. 2). Bisphenol-C ( $30 \times 10^{-3}$  mol) was suspended and partially dissolved in water (150 mL) containing sodium hydroxide ( $66 \times 10^{-3}$  mol). IPCl ( $30 \times 10^{-3}$  mol) and TPC ( $30 \times 10^{-3}$  mol) were dissolved in dry dichloromethane (200 mL). Both solutions were cooled in a refrigerator (2 °C) for approximately 20 h. Afterwards, both solutions were mixed and rapidly stirred for 2 h under cooling with ice. Stirring was then continued for 20 h without cooling. The reaction mixture was then diluted with dichloromethane (100 mL), the water phase was removed and the organic phase was washed with water (150 mL). After drying with a small amount of sodium sulfate, the organic phase was concentrated to a volume of approximately 80 mL and poured into methanol (800 mL). The precipitated polyester was isolated by filtration and dried at 50 °C in vacuo.

Experiments 1, 3 and 4 were performed analogously, but in the case of No. 4, the reaction mixture was diluted with 200 mL of dichloromethane and 100 mL of water prior to the phase separation.

Analogous polycondensations were performed with larger amounts of PT-catalyst.

4.2.2.2. Polycondensation in Homogeneous Solution (No. 1 and 2, Table 3). Bisphenol-C ( $30 \times 10^{-3}$  mol) and IPCl ( $30 \times 10^{-3}$  mol) were dissolved in dry dichloromethane (180 mL) and cooled to approximately 4°C. A solution of pyridine ( $120 \times 10^{-3}$  mol) in dichloromethane (20 mL) was added rapidly (but dropwise). The reaction mixture was stirred without cooling for 20 h, concentrated to a volume of approximately 80 mL and precipitated into methanol. Experiments No. 6 and 7 were performed analogously. Analogous polycondensations were conducted with triethyl amine (No. 3 and 4.)

#### 4.2.3. Measurements

The MALDI-TOF mass spectra were measured on a Bruker “Smart-beam” ( $\lambda = 355 \mu\text{m}$ ) spectrometer in the linear mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions using dithranol as the matrix and potassium trifluoroacetate as the dopant. The SEC measurements of the poly(hexanediol isophthalate)s were measured on

a chromatograph of Polymer Laboratories, Varian, Inc. equipped with a RI detector "Shodex 101". A combination of three columns was used: 1 × 5 μm Mixed C and 2 × ResiPore from Polymer Laboratories, Varian, Inc., THF served as the eluent at 30 °C and commercial polystyrene standards were used for calibration. The SEC measurements of the poly(bisphenol-C isophthalate) were performed in chloroform at 30 °C using a home-made apparatus consisting of a Merck-Hitachi L-7100 pump, an ERC 7510 RI detector and a Merck L-5025 column thermostat. A combination of two PSS mixed-bed columns (B 10 μ) was used together with a sample concentration of 5 mg L<sup>-1</sup>. The Win GPC Unity software served for evaluation of the elution curves.

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