Cyclic and Multicyclic Polymers by Three-Dimensional Polycondensation

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CONSPECTUS

The recent confirmation that polycondensations (and other step-growth polymerizations) of difunctional monomers involve cyclization reactions at any concentration and at any stage of the polymerization also has consequences for three-dimensional polycondensations on multifunctional monomers. It is demonstrated that tree-shaped (hyperbranched) oligomers are gradually transformed into star-shaped polymers with a cyclic core, when the conversion increases. Polycondensations of "$a_2 + b_3$" or "$a_2 + b_4$" monomer combinations yield multicyclic polymers, when gelation can be avoided. This new architecture may be subdivided into three groups: perfect multicycles free of functional groups, multicycles having b functions, and multicycles having "a" groups. The concrete examples discussed in this Account mainly concern polyethers and polyesters.
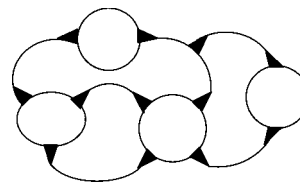
Introduction

Step-growth polymerizations are a group of polymer syntheses that, in contrast to chain-growth polymerizations, have the characteristic that all reactive species, monomers, oligomers, and polymers, can react with each other at any time and at any stage of the polymerization process. Step-growth polymerizations are usually subdivided into polycondensations and polyadditions. According to the standard terminology of organic and inorganic chemistry, each reaction step of a polycondensation involves elimination of a small molecule, such as water, methanol, or HCl. The classical theory of step-growth polymerizations, as present in all textbooks of polymer science, goes back to the work of Carothers[1] and Nobel prize laureat Flory.[2] Their experimental and theoretical work represents one of the most important contributions to polymer science (and biochemistry) ever made, culminating in the synthesis of nylons, the first man-made fibers. Despite its enormous merits, the classical theory of step-growth polymerizations has the shortcoming that it ignores the role of cyclization reactions. At the time of

Carothers' and Flory's work, it proved difficult to synthesize macrocycles consisting of more than eight atoms in a ring and analytical methods allowing for the detection of cyclic oligomers or polymers in complex reaction mixtures did not exist. Furthermore, Flory concluded from calculations of chain conformations:[2]

> "However, in ordinary bifunctional condensations (no diluent) the primary product from monomers (or dimers) of fifteen or more members is almost exclusively linear polymer. This results from the statistical improbability that the ends of a large chain of atoms connected by valence bonds, about there is free rotation, will meet."

In the years 1970−1975, Stepto et al.[3] and Gordon et al.[4] published speculative calculations suggesting that cyclization competes with each growing step at least, when step-growth polymerizations are conducted at low or moderate monomer concentrations. Cyclic polymers were meanwhile synthesized by numerous research groups[5,6] using low monomer concentrations according to the "Ruggli−Ziegler dilution prin-

ciple". Furthermore, Tezuka and co-workers[7,8] prepared cyclic polymers in high yields via electrostatic interaction from monomers having charged functional groups. However, all of these cyclization studies are not in contradiction to the classical theory of Carothers and Flory. After 1995, the availability of fast atom bombardment (FAB) and matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) mass spectrometries has considerably improved the experimental situation, and the authors' recent work[9−15] has resulted in the following conclusion. Cyclization competes with chain growth at any stage of a polycondensation and at any concentration (even in bulk), so that a clean polycondensation yields 100% cycles at 100% conversion. Because any kind of cyclization consumes functional groups, it reduces the efficiency of chain growth. Equation 1 summarizes the correlation of the average degree of polymerization (DP) with the conversion "p" under the influence of cyclization (a graphical illustration of this equation was presented in ref 9)

$$DP = \frac{1}{1 - p(1 - X^{-a})} \quad a = V_{pr}/V_{cy} \quad (1)$$

where V_{pr} is the rate of chain growth, V_{cy} is the rate of cyclization, and X is a constant, with values >1.0.

At this point, it should be mentioned that, in step-growth polymerizations, the conversion needs to be defined as the consumption of functional groups (eq 2) and not as a consumption of monomers in contrast to chain-growth polymerizations

$$p = \frac{N_o + N_t}{N_o} \quad (2)$$

where N_o and N_t are the number of functional groups at the beginning or at a later state of the polycondensation. Equation 3 is a direct consequence of eq 2 and indicates how the molar concentration of all active linear species (i.e., monomers, oligomers, and polymers) decreases with higher conversions

$$[L_a]_t = [L_a]_o(1 - p) \quad (3)$$

where $[L_a]$ is the molar concentration of all linear species bearing one functional "a" group. At 100% conversion, all linear species have vanished by transformation into cycles.

This new theory of step-growth polymerization was at first elaborated for two-dimensional systems, meaning polycondensations of "ab" or "$a_2 + b_2$" monomers. The present Account was aimed at discussing the influence of the cyclization reaction on three-dimensional polycondensations

SCHEME 1. Homopolycondensation of an "ab_2" Monomer Forming a Tree-Shaped (Hyperbranched) Polymer
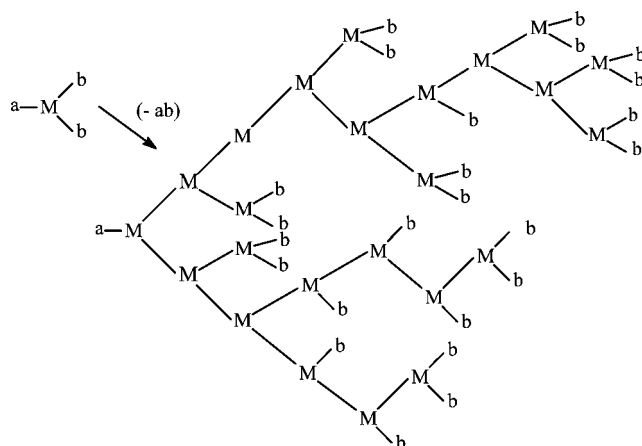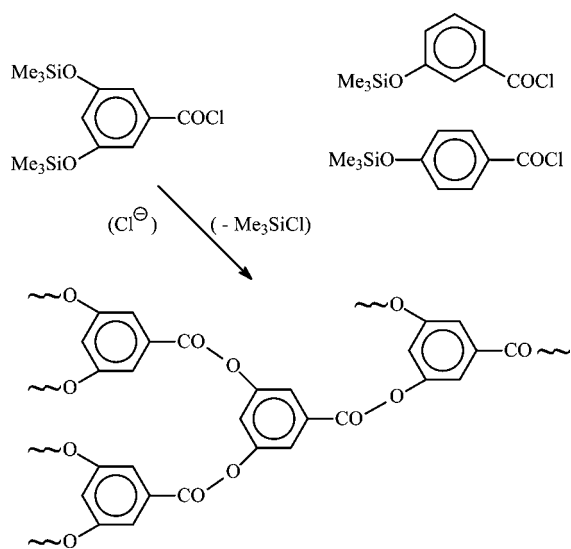

(Flory's terminology[2]). Three-dimensional polycondensations may be classified into those based on "ab_n" monomers and polycondensations based on "$a_2 + b_n$" monomers. In this terminology, "a" and "b" mean functional groups that can react with each other, whereas "a" cannot react with "a" and "b" cannot react with "b".
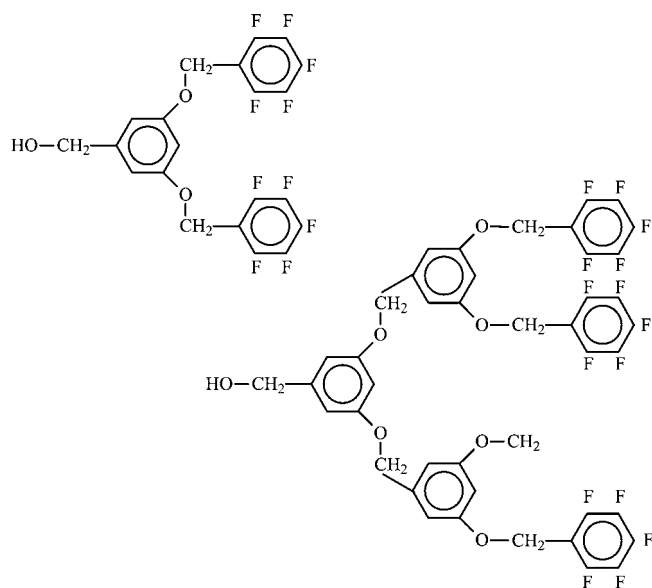
Polycondensations of "ab_n" Monomers

Branched homo- and copolymers with a tree-shaped architecture, later called "hyperbranched", are an "invention" of the evolution of life in the form of polysaccharides, such as amylopectines or glycogen. A first experimental approach trying to copy nature by simple copolycondensation of "ab" and "ab_2" monomers was published by the author,[16] who studied copolycondensations of 3,5-bistrimethylsiloxybenzoyl chloride (**1**) with 3- or 4-trimethylsiloxybenzoyl chloride (**2**, **3**, Schemes 1−3). This synthetic approach to hyperbranched (co)polyesters was later elaborated by several research groups[17−21] in more detail, mainly concentrating on the homopolycondensation of **1**. However, prior to any experimental work, "ab_n" polycondensations were theoretically analyzed by Flory.[2] His "cascade theory" was, in turn, another source of stimulation for further theoretical and experimental studies. Therefore, it is a distortion of historic facts, when the origin of studies of hyperbranched polymers is attributed to "the search of simpler methods to prepare dendrimer-like polymers...".[22]
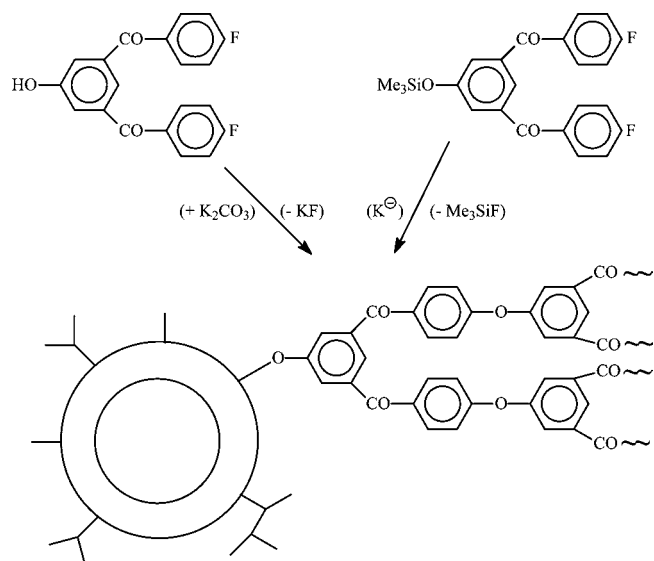
Further theoretical studies of "ab_n" polycondensations mainly concentrated on calculations of molecular-weight distributions (MWDs) and degree of branching (DB).[23−32] With the exception of ref 32, which contains unclear and inconsistent experimental data, none of those publications considers a decisive influence of cyclization reactions on the course of "ab_n" polycondensations.

SCHEME 2. Copolycondensation of an "ab₂" and "ab" Monomer
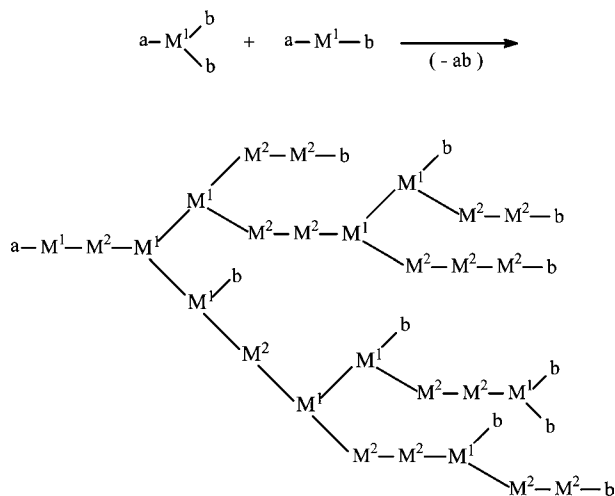
SCHEME 3. Monomers (and Reaction Pathway) Used for the Preparation of Hyperbranched Homo- and Copolyesters in Refs 18−23

SCHEME 4. Monomers Used for the Preparation of Hyperbranched Polymers Including Cyclic Oligomers
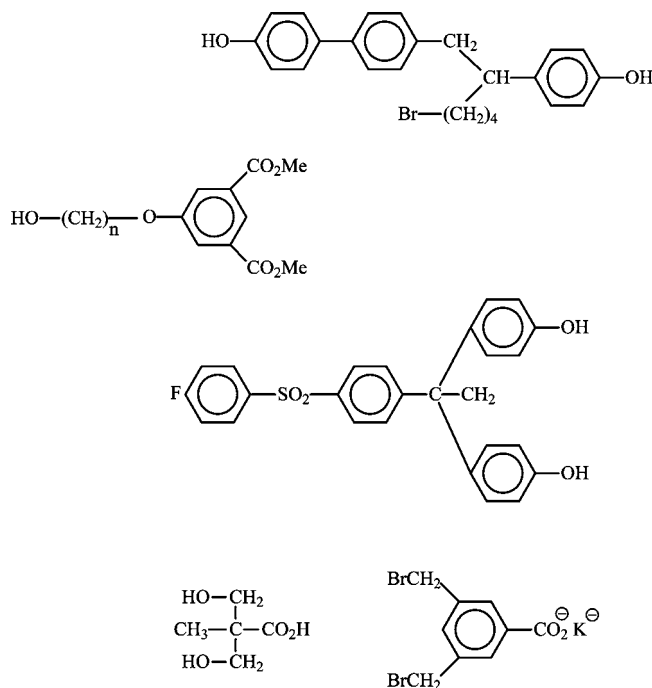
SCHEME 5. Monomers Used for the Preparation of Hyperbranched Oligo(ether ketone)s with a High Content of Oligomers Having a Cyclic Core[43]

Also, all experimental studies published before 1994 and most works published afterward[33−36] have in common that their authors did not care about the influence of cyclization reactions. Percec et al.[37] were the first reporting that part of their hyperbranched oligomers had a cyclic structure (first formula in Scheme 4). A few years later, other research groups studying polycondensations of the monomers summarized in Scheme 4 also reported on the formation of cyclic oligomers.[38−41] However, when Gooden et al. studied polycondensations of perfluorinated monomers (Scheme 5),[42] they found rather low molecular weights and up to 80% of their reaction products had a cyclic core. The numerous C−F groups neighboring the OH group obviously favor efficient cyclizations. Finally, the author studied polycondensations of 1,3-bis(4-fluorobenzoyl)phenol or its silylated version (Scheme

6).[43] Upon variation of the reaction medium and reaction conditions, the lowest molecular weight was obtained in sulfolane. The MT mass spectrum evidenced that a particularly clean polycondensation with high conversion had occurred, yielding a product almost exclusively consisting of cycles. These findings and the results obtained from two-dimensional polycondensations now justify the following conclusions: (1) Cyclization limits the chain growth, so that eq 1 is also valid

SCHEME 6. Formation of Sun-Shaped Poly(ether ketone)s by Polycondensation of 1,3-Bis(4-fluorobenzoyl)phenol or Its Trimethylsilyl Derivative[44]

SCHEME 7. Isomers of the (Perfect) Multicycles $B_{1/2N}CN$ Derived from Even-Numbered Oligomers of "b_3" Monomers[a]

B_1C2

B_2C4

B_3C6

[a] The triangles represent the b_3 unit.

for "ab_n" polycondensations. (2) The definition of conversion (eq 2) is valid, when restricted to "a" groups. (3) When conversion is increased, more and more tree-shaped oligomers and polymers are transformed into star-shaped polymers having a cyclic core and branched side chains (as exemplarily illustrated in Scheme 6). According to eq 4, which is an analogue of eq 3, all reaction products have a cyclic core at 100% conversion
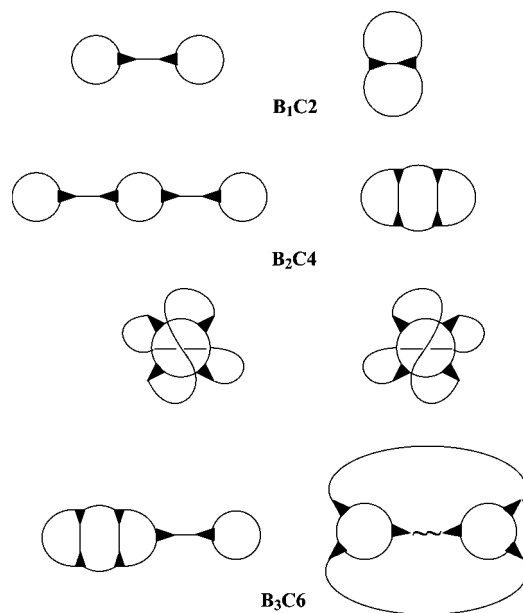
$$[H_a]_t = [H_a]_o(1 - p) \qquad (4)$$

where $[H_a]$ is the molar concentration of all "hyperbranched" species (including "ab_n" monomers) having one "a" group. In other words, all "ab_n" polycondensations aim at star-shaped (or sun-shaped) polymers as the final architecture. The average size of the cyclic core increases with the conversion.

Polycondensations of "$a_2 + b_3$" Monomers

Polycondensations of "$a_2 + b_3$" monomers have a long history because polycondensations of glycerol with dicarboxylic acids or cyclic anhydrides were studied by members of the U.S. General Electric Co. since 1914.[44−46] Those experiments and the later experimental (and theoretical) studies of Flory[2,47] all concerned a feed ratio of 1.5:1.0, which may be called equifunctional stoichiometry. It was found that, regardless of the "a_2" monomers and the reaction conditions, gelation occurred around 70% conversion.

Later studies of other research groups went in two different directions. Either the polycondensations were performed with equifunctional stoichiometry but under extreme dilution while bicyclic di- or trimers were isolated,[48,49] or polyconden-

sations were conducted with equimolar stoichiometry at high concentrations to prepare (hyper)branched polymers. In almost all papers dealing with equimolar "$a_2 + b_3$" polycondensations, characterization of the reaction products by MT mass spectroscopy is lacking and, thus, it is not clear if the isolated reaction products indeed possess the expected hyperbranched structure free of cyclic elements.[34−36]

It was the purpose of the author's work to find out if it is feasible to perform equifunctional "$a_2 + b_3$" polycondensations with almost quantitative conversion under conditions avoiding gelation. Such polycondensations, when successful, should yield soluble multicyclic polymers, which represent a new architecture. Prior to the discussion of experimental results, the simplified structural formulas and letter symbols (sum formulas) used for the denomination of multicycles should be explained. The structural formulas are constructed from triangles representing the "b_3" units, as illustrated in Schemes 7−9. The multicycles may be subdivided into four classes: (1) Perfect multicycles free of any functional groups (Scheme 8). Such multicycles can only exist for even-numbered degrees of polymerization. They are the result of equifunctional polycondensations under (almost) ideal reaction conditions. (2) Multicycles having unreacted "b" groups. Such multicycles are the normal reaction products of odd-numbered DPs, as illustrated in Scheme 9. They will also be formed for even-numbered DPs, when the feed ratios are below 1.5:1.0. (3) Multicycles having unreacted "a" groups (Scheme 9) are the consequence of polycondensations with

SCHEME 8. b-Functional Multicycles Derived from Odd-Numbered Oligomers of "b₃" Monomers
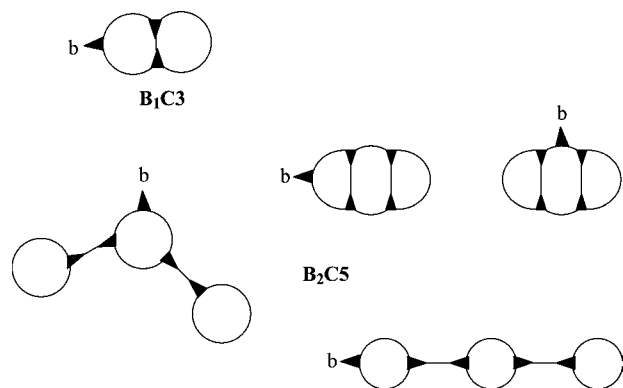
SCHEME 9. Examples of Multicycles Having Pendant "M-a" Units[a]

B₃C4 or **B₁C4 − a₂**   **B₃C5** or **B₂C5 − a**
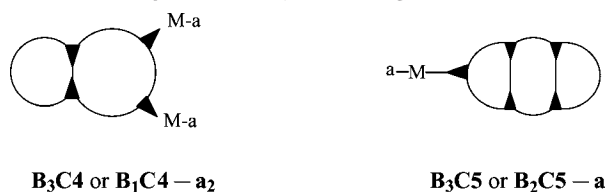
[a] The addition of M indicates that the functional "a" group is not directly attached to the b₃ unit.

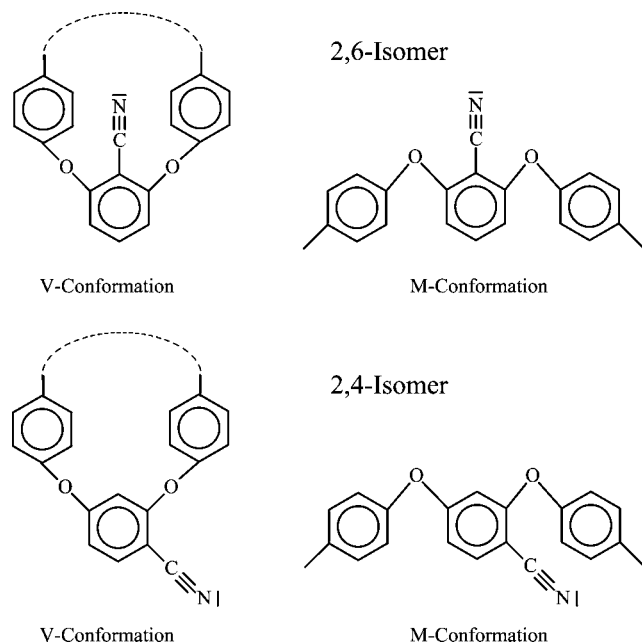feed ratios >1.5:1.0. (4) Multicycles having both free "a" and "b" groups indicate incomplete conversions.

The sum formulas B$_n$CN presented in Schemes 7−9 (and in the text below) are useless for a distinction of isomers, but they are useful for assigning mass peaks, because FAB and MT mass spectra do not allow for a differentiation of isomers. In these formulas, C stands for circular structure and N is the DP (i.e., one a + one b moiety). B means bridge unit resulting from incorporation of an additional "a₂" monomer, which forms a bridge across a cycle or connects two cycles. In a two-dimensional drawing, a multicycle consists of B$_n$ + 1 cycles.

Multicyclic polymers reported thus far mainly encompass aromatic polyethers. The first studies in this direction were undertaken with silylated phloroglucinol[50] (Scheme 10) or silylated 1,1,1-tris(4-hydroxyphenyl ethane) (THPE)[51] as nucleophilic "b₃" monomers. The trimethylsilyl derivatives were preferentially used, because they effect under the alkaline reaction conditions a better protection against oxidation and yield cleaner polycondensations. When silylated phloroglucinol was reacted with 4,4′-difluorodiphenyl sulfone at an initial monomer concentration of 0.12 mol/L, the reaction products were soluble up to feed ratios of 1.3:1.0.[50] The MT mass spectra indicated the formation of various multicycles having free OH groups (after hydrolytic removal of the silyl groups). Remarkably, even at a 1.0:1.0 feed ratio, the non-cyclic oligomers and polymers were a minority and simple

SCHEME 10. Phloroglucinol or THPE and Various Difluoroaromatics Used for Syntheses of Multicyclic Polyethers
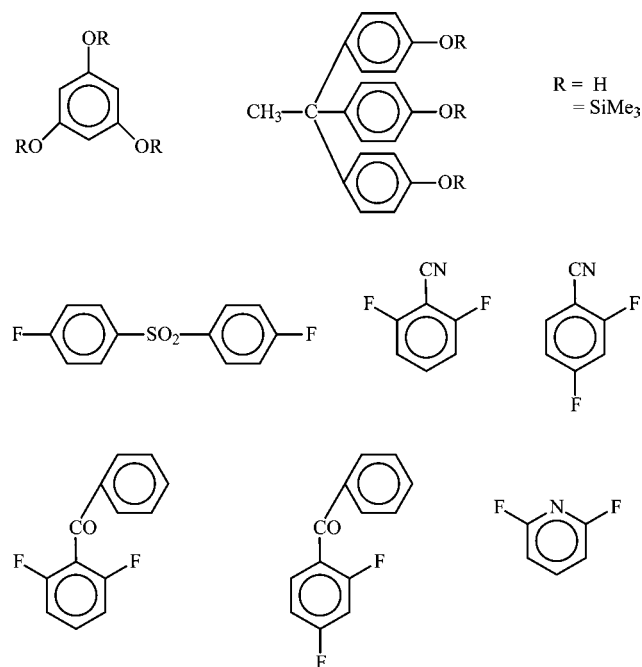
cycles (CN) were the prevailing products. Under the same conditions, condensations of DFDPS with silylated or free THPE ended up with gelation at feed ratios above 1.1:1.0.[51] Even at this low feed ratio, the reaction product almost completely consisted of cyclic and multicyclic polyethers. When DFDPS was polycondensed with free THPL at a monomer concentration of 0.05 mol/L, all reaction products were soluble regardless of the feed ratio, and at feed ratios around 1.5:1.0, the perfect multicycles were the predominant reaction products.[52]
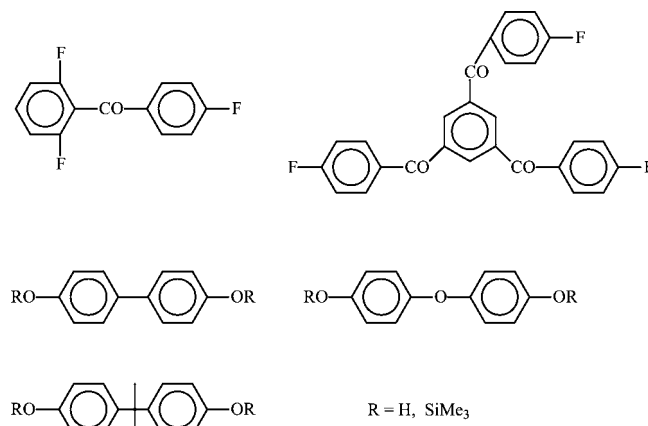
Particularly interesting were polycondensations of silylated THPE with 2,6- and 2,4-difluorobenzonitrile (Scheme 10).[53] At a THPE concentration of 0.12 mol/L, the 2,6 isomer yielded gels at a feed ratios >1.1:1.0. However, at the same monomer concentration, all polycondensates were soluble up to feed ratios of 1.5:1.0, when the 2,4 isomer was used. This conspicuous difference between both isomers was explained in terms of two conformations labeled V and M (Scheme 11). It was assumed that the V conformation favors cyclization far more than the M conformation, as indicated by a dotted line. Computer modeling of conformation energies revealed that, in the case of the 2,6 isomer, the V conformation possesses the highest energy and the M conformation possesses the lowest energy, thereby favoring chain growth and gelation. The reason for this energy distribution consists of the repulsive forces between the electrons of the nitrile group and the π electrons of the phenoxy groups. The opposite trend was found for the 2,4 isomer, which favors V-like conformations

SCHEME 11. Comparison of V and M Conformations or 2,6- and 2,4-Substituted Benzonitrils

2,6-Isomer

V-Conformation   M-Conformation

2,4-Isomer

V-Conformation   M-Conformation

SCHEME 12. 2,6,4′-Trifluorobenzophenone and 1,3,5-Tris(4-fluorobenzoyl)benzene and Various (Silylated) Diphenols Used for Syntheses of Multicyclic Polyethers

R = H, SiMe$_3$

and, thus, cyclizations. This hypothesis also proved to be valid when THPE was polycondensed with 2,6- and 2,4-difluorobenzophenone.[54]

Polycondensations of (silylated) THPE with 2,6-difluoropyridine were of interest for two reasons. First, it should be elucidated if the cyclization tendency of 2,6-difluorobenzonitrile or that of the 2,4 isomer. Second, incorporation of a tertiary nitrogen in the repeat units should allow for a quarternization with strong alkylating agents and, thus, for syntheses of multicyclic polyelectrolytes. Successful alkylation of linear or cyclic poly(pyridine ether)s had been reported before.[55] Polycondensations of 2,6-difluoropyridine with silylated bisphenol A had also indicated before that the cyclization tendency of poly(pyridine ether)s may be extraordinarily high.[56] This tendency was confirmed by the polycondensations with THPE, which yielded soluble multicycles regardless of the feed ratio at a THPE concentration of 0.12 mol/L.[57] A remarkable result of that study was a MT mass spectrum of the 1.5:1.0 polycondensate, which exclusively displayed mass peaks of perfect multicycles up to a mass around 32 000 Da, corresponding to a DP of 78. This mass spectrum proved that the formation of the multicyclic architecture is not limited to oligomers.

All syntheses of multicyclic polyethers discussed above have in common that the "b$_3$" monomer was a phenol and, thus, a nucleophilic reactant. In two more publications, the inverse concept was realized. Activated trifluoro-aromatics, namely, 2,6,4′-trifluorobenzophenone[58] and 1,3,5-tris(4-fluo-

robenzoyl)benzene,[59] were used as electrophilic reaction partners of several diphenols (Scheme 12).

As expected, the stereochemistry and flexibility of the diphenol played a key role in the success of these polycondensations. With the stiff, linear 4,4′-dihydroxybiphenyl gelation occurred at a feed ratio of 1.1:1.0. With 4,4′-dihydroxydiphenyl ether, gelation occurred only at feed ratios >1.3:1.0 and bisphenol A yielded soluble multicycles even with equifunctional stoichiometry. Because the bond angle of diphenyl ether is around 123 ± 1° and that of bisphenol A is around 110 ± 1°, these results demonstrate that relatively small changes in the steric demands of the diphenols have conspicuous consequences for the formation of soluble multicycles.

The polycondensations of both trifluoroketones with diphenols have in common that, at a feed ratio of 1.5:1.0, coconversion close to 100% was not achieved. None-the-less, the perfect multicycles were the largely prevailing products in the reaction mixture. The multicycles derived from 2,6,4′-trifluorobenzophenone and bisphenol A presented the rare case of a good solubility in neat chloroform or dichloromethane. Therefore, size-exclusion chromatography (SEC) measurements were feasible, which showed that the sample with the highest molecular weight contained a fraction with masses in the range of 10^6–10^8 Da.[58] Light scattering confirmed a weight average molecular weight (M_w) around 2×10^6 Da. This sample crosses the borderline between soluble nano- and microgels. In this connection, polycondensations of pentafluorobenzonitrile should be mentioned. The nitrile groups only activate the three C–F groups in *ortho* and *para* positions, and all attempts to achieve a clean substitution of all five F atoms be means of phenoxide ions indeed failed. However, polycondensations with diphenols in a molar ratio of 3:2 (a$_2$/b$_3$) were

SCHEME 13. Trimesoylchloride and Various Diols Used for the Preparation of Multicyclic Poly(ether ester)s
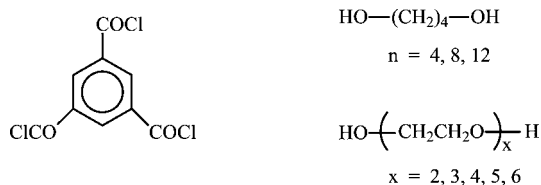
successful and yielded perfect multicycles[60] (containing two C−F groups per repeat unit).

For the preparation of multicyclic polyesters, trimesoyl chloride seemed to be a useful "b_3" monomer and various aliphatic diols served as reaction partners (Scheme 13), in combination with pyridine as a catalyst and HCl as an acceptor.[61] At concentrations of trimesoyl chloride down to 0.04 mol/L, the alkane diols yielded gels regardless of their lengths. In the case of monodisperse oligo(ethylene glycol)s, the lengths played a decisive role. Soluble multicycles were obtained from tri- and tetra(ethylene glycol)s at the relatively high concentration of 0.40 mol/L, whereas the longer diols produced gels. The isolated multicyclic polyesters proved to be stable against neutral or slightly acidic water at 25 °C, quite analogous to poly(ethylene terephthalate). This property and the ether cycles of different size, which exist in such a nanogel, have the consequence that the poly(ether ester)s may be used as cryptands for alkali metal ions. They solubilized all alkali metal benzoates in dioxane without any selectivity. From this point of view, they are the counterparts of the highly selective crown ethers.

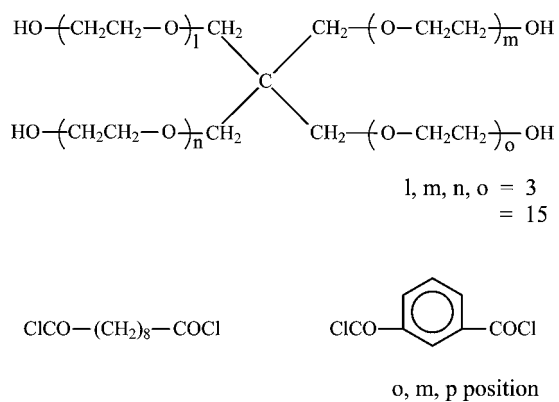## Polycondensations of "$a_2 + b_4$" Monomers under Kinetic Control

The first polycondensation of an "$a_2 + b_4$" monomer combination was reported by Flory,[2] who used mixtures of dicarboxylic acids and pentaerythritol as starting materials. Feed ratios of 2.0:1.0 (equifunctional) and polycondensations in bulk had the consequence that gelation occurred around 60% conversion. A systematic study of syntheses and characterization of multicyclic polymers based on "$a_2 + b_4$" monomers was recently launched by the author. In principle, these multicycles may be described by simplified structural formulas and sum formulas paralleling those introduced above for "$a_2 + b_3$" polycondensates (Schemes 7−9). However, there also exists a couple of characteristic differences that need explanation. In the case of "$a_2 + b_4$" polycondensations, the number of isomers very much depends upon the stereochemistry of the "b_4" monomer, as illustrated in Scheme 14. Scheme 15 demonstrates for oligoethers of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl spirobisindane (TTSBI) that many more isomers of

SCHEME 14. Isomeric Bicycles Derived from "b_4" Monomers with Different Stereochemistry
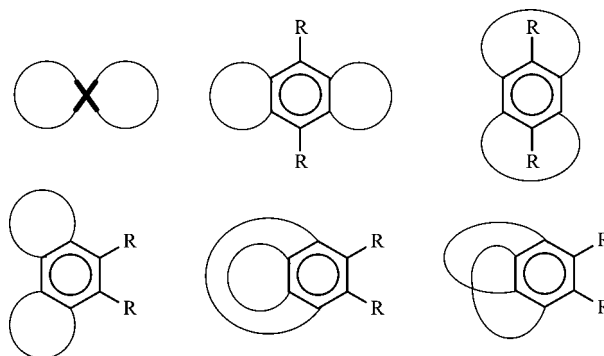
SCHEME 15. Isomers of Tricyclic Dimers Derived from TTSBI
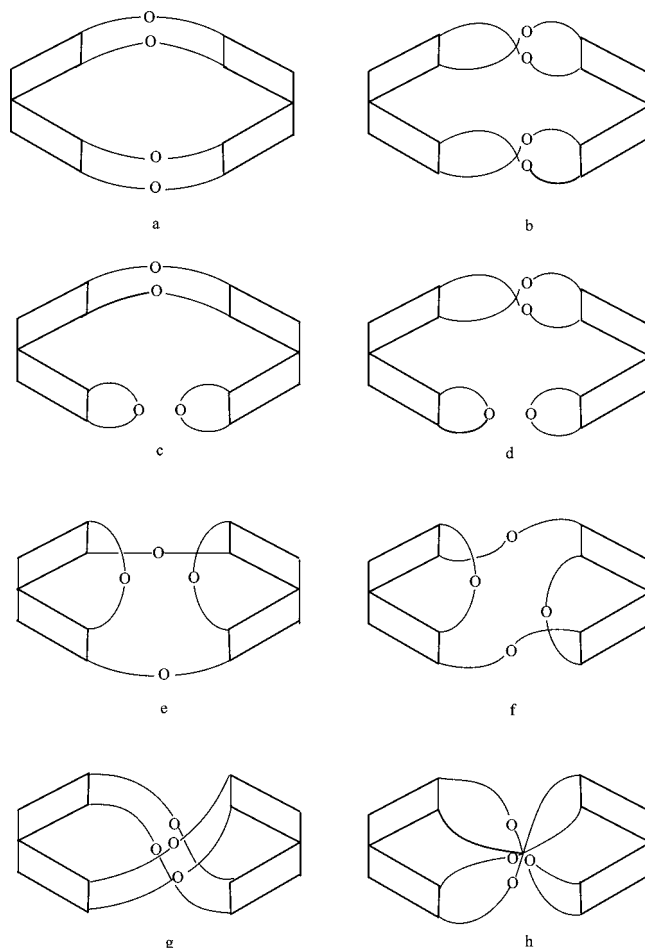
"b_4" dimers exist in contrast to two isomers of "b_3" dimers (see B_1C_2 in Scheme 7).

Among the least expensive commercial "b_4" monomers are pentaerythritol and its derivatives. Therefore, the possibility of synthesizing soluble multicyclic polyesters from such commercial "b_4" monomers was studied in detail. Because pentaerythritol itself is insoluble in common inert

SCHEME 16. Ethoxylated Pentaerythritol and Various DADs Used for Syntheses of Multicyclic Poly(ether ester)s

l, m, n, o = 3
= 15

o, m, p position

SCHEME 17. Syntheses of Multicyclic Polythioesters from Pentaerythritol Tetramercaptoacetate

n = 4, 6, 8, 10

+ higher multicycles

SCHEME 18. TTSBI and Various DADs Used for Syntheses of Multicyclic Polyesters
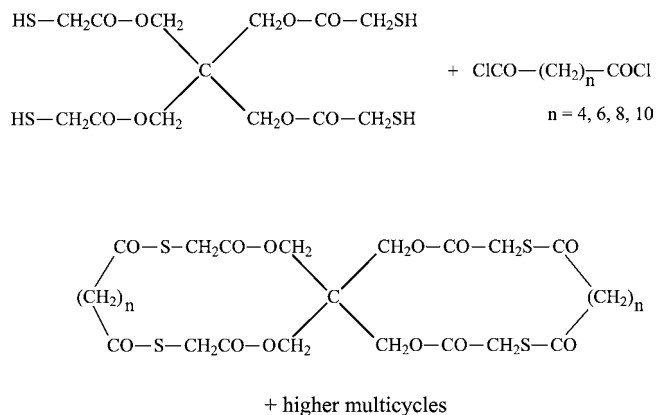

n = 3, 4, 5, 6

n = 4, 6

solvents, polycondensations with dicarboxylic dichlorides under mild conditions were not feasible.

Soluble derivatives of pentyerythritol are the ethoxylated tetraols outlined in Scheme 16. The favorization of loops and cycles by aliphatic ether groups became evident, when ethoxylated pentaerythritol was polycondensed with various dicarboxylic acid dichlorides (DADs) (Scheme 16).[62] Despite the shorter distance between the OH group, the tetraol having 3 ethoxy groups was more prone to gelation than the compound having 15 ethoxy groups. Sebacoyl chloride failed to yield multicycles, whereas polycondensations with phthaloyl chloride were successful. Because alkane chains prefer the all-trans conformation, difunctional reagents based on alkane chains are relatively unfavorable for cyclization reactions despite the low rotational barrier of the C–C bonds. The cyclization tendency of the aromatic DADs decreased, as expected, in the following order: phthaloyl > isophtholoyl > terephthaloyl chloride.
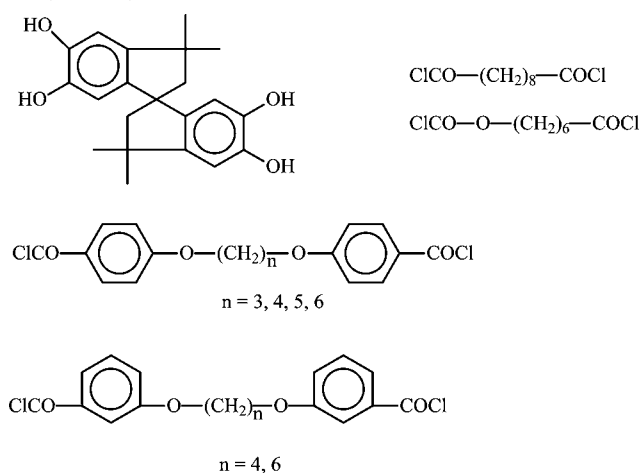
Numerous attempts were made to prepare multicyclic polythioesters from pentaerythritol tetramercaptoacetate (Scheme 17).[63] However, even at the low concentration of 0.025 mol/L, all experiments with aromatic DADs ended with gelation. In contrast, soluble multicycles were obtained by polycondensation with adipoyl, suberoyl, sebacoyl, and 1,10-decane dicarbonyl chloride. With suberoyl and sebacoyl chloride, completely soluble reaction products were achieved, even at 0.025 mol/L. In other words, the cyclization tendency of this system passed a maximum at a medium length of ADAs. Furthermore, the correlation between cyclization and aliphatic or aromatic dicarboxylic acids was opposite that observed for polycondensations of ethyxylated pentaerythritols (Scheme 16).

Further multicyclic polyesters were prepared from TTSBI and various DADs (Scheme 18).[64] With sebacoyl chloride or 1,6-hexane diol bischloroformiate, partial or total cross-link-

ing was observed at concentrations down to 0.02 mol/L. However, soluble multicycles were obtained with both classes of semi-aromatic dichlorides (Scheme 18), and with the *meta*-linked dichlorides, soluble multicycles were also formed at 0.04 mol/L. The resulting multicyclic polyesters had relatively high molar masses compared to other "$a_2 + b_4$" polycondensates.

TTSBI also proved to be an useful "b_4" monomer for syntheses of multicyclic polyethers. Two different synthetic methods were successful. First, alkylation of TTSBI with the bistosylates of di- or tri(ethylene glycol) (Scheme 19).[65] The resulting polyethers showed the typical properties of crown ethers or kryptands and solubilized alkali metal benzoates in dioxane or tetrahydrofuran without selectivity for the cation. Second, thermostable fully aromatic multicyclic poly(ether)s were obtained by polycondensation of TTSBI with 4,4'-difluoro- or dichlorodiphenyl sulfone and 4,4'-bis(4-chlorophenyl sulfonyl) biphenyl (Scheme 20). High fractions of perfect multicycles were only achieved with the third "a_2"

SCHEME 19. Spirocyclic Oligoethers Prepared (Together with Higher Multicycles) by Alkylation of TTSBI with Bistosylated Di- or Tri(ethylene glycol)

n = 0 or 1
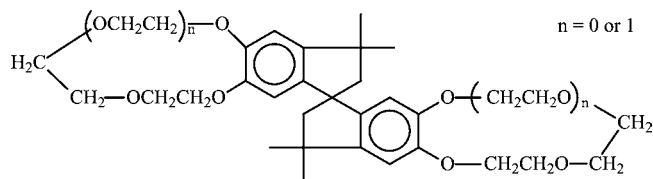
SCHEME 20. Monomers Used for the Preparation of Multicyclic Poly(ether sulfone)s
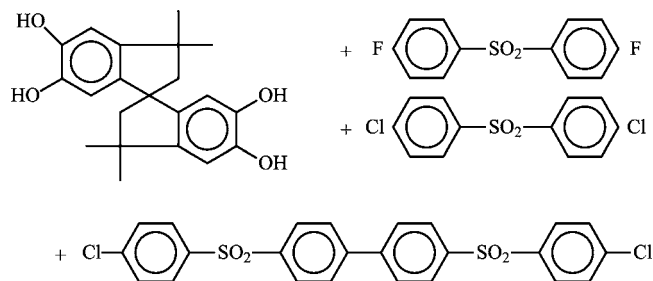
SCHEME 21. Isomeric Tetrafluorodicyanobenzenes and Various Diphenols Used for Syntheses of Multicyclic Polyethers

SCHEME 22. Syntheses of Spiro- and Multicyclic Oligo- and Polyethers from Tetra(bromomethyl)methane

+ multicyclic polyethers
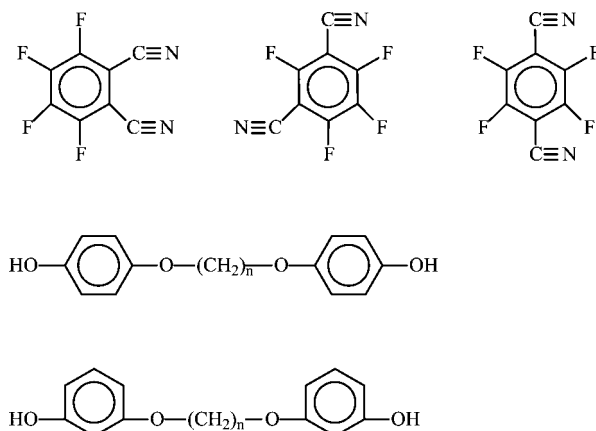
monomer,[66,67] apparently because cyclization reactions of the shorter "a_2" monomers are sterically hindered.

Further aromatic multicyclic polyethers were prepared from the three isomeric dicyanotetrafluorobenzenes and flexible diphenols (Scheme 21). The 1,2- and 1,4-dicyano compounds allowed for a clear and complete substitution of all four F atoms, so that almost exclusively perfect multicycles were formed at a feed ratio of 2:1 (a_2/b_4; Scheme 21).[68,69] However, the nitrile groups of the 1,3 isomer only activate the three C−F groups in *ortho* and *para* positions, and a high conversion of the fourth C−F was never achieved. However, when the polycondensations were performed with a 3:2 feed ratio, a high yield of perfect multicycles corresponding to "$a_2 + b_3$" polycondensates was isolated. In other words, the 1,3-dicyanotetrafluorobenzene proved to be a useful "b_3" monomer.[69]

Soluble spiro- and multicyclic oligo- and polyethers were also obtained from tetra(bromomethyl)methane.[70] The success of these polycondensations very much depended upon the structure of the diphenols. Whereas most diphenols yielded gels, *tert*-butylcatechol yielded mainly the monomeric spirocycle (Scheme 22), as evidenced by FAB mass spectrometry. Longer flexible diphenols yielded perfect multicyclic polyethers (Scheme 22).

Finally, a recent study by Nishikubo and co-workers should be mentioned, who used resorcinol as "a_2" and pentanedial (or other aliphatic bisaldehydes) as "b_4" monomers.[71,72] Under optimized reaction conditions, a crystalline, monodisperse, multicyclic oligomer precipitated from the reaction mixture (Scheme 23). This polyhydroxy compound was quantitatively transformed into a *tert*-butoxycarbonyl derivative, which showed good solubility in various organic solvents. Recrystallization yielded a pure product, of which the X-ray crystal analysis proved the structure nick-named "noria" (the Latin word for water-wheel).

Polycondensations of "$a_2 + b_4$" Monomers under Thermodynamic Control

All polycondensations discussed above had in common that they proceeded via irreversible reaction steps. Hence, the competition between cyclization and chain growth represented a kinetic competition. However, in the fields of ring-opening polymerization and polycondensation, polymerization pro-

SCHEME 23. Synthesis of a Monodisperse Multicyclic Oligomer Called "Noria" from Resorcinol and Pentanol
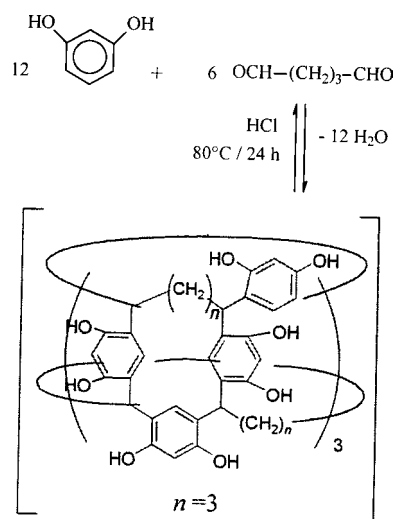
SCHEME 24. Thermodynamically Controlled Polycondensations of Ge-Tetramethoxide with Oligo(ethylene glycol)s

+ soluble higher multicycles
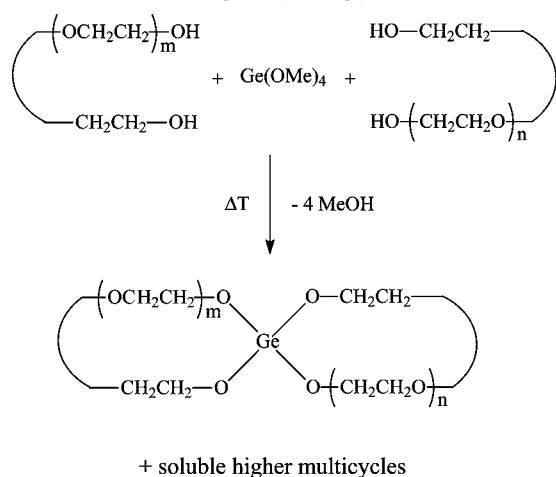
cesses exist that involve rapid equilibration (e.g., transesterification). In these cases, the composition of the reaction product reflects at any time the thermodynamically most favorable situation of the entire system. This situation stimulated the author to find out if spiro- and multicyclic oligomers and polymers can be prepared under thermodynamic control.

When ethoxylated pentaerythritol is polycondensed with dibutyltin dimethoxide in concentrated toluene solution with complete removal of the liberated methanol, a syrupy product is obtained, which remains syrupy and transparent at temperatures above 60 °C, even when heated for several days (Scheme 24).[73,74] For two reasons, this polycondensation involves rapid equilibration. First, the condensation steps are reversible as long as methanol is present in the reaction mixture. Second, it is known from numerous tin[IV] alkoxides that strong donor−acceptor interactions exist between the O elec-

trons and the free orbitals of tin, with the consequence that, if not sterically hindered, a rapid exchange of alkoxide groups takes place.

The second example concerns germanium tetraalkoxides. It was known from the work of Mehrotra et al.[75] that polycondensations of $Ge(OMe)_4$ with even-numbered alkane diols yield solid networks regardless of the chain length. However, 1,3-propane diol gave a well-defined soluble spirocycle based on two six-membered cycles. When the author polycondensed $Ge(OMe)_4$ with various syrupy oligoethylene glycols, soluble reaction products were obtained in all cases.[76] Because, as mentioned before, aliphatic ether groups favor formations of loops and cycles for kinetic and thermodynamic reasons, it is not surprising that polycondensations of $Ge(OMe)_4$ with oligo(ethylene glycol)s favor spiro- and multicycles at the expense of networks. A large number of smaller molecules represents a much higher level of entropy than an infinite network, and thus, these polycondensations are entropy-driven, when the reaction enthalpy is close to zero. In the case of alkane diols, the formation of small cycles requires unfavorable gauche conformations and, in certain cases, also *trans*-annular interactions, which may be absent in a network. Therefore, the formation of networks from alkane diols may be favored by a negative reaction enthalpy relative to the formation of multicycles. Polycondensations of various metal tetralkoxides with long oligo(ethylene glycol)s also yielded soluble multicycles.[77]

Conclusions

The permanent competition of cyclization with chain growth has a strong influence on all important aspects of three-dimensional polycondensations: (1) It modifies the architecture in the direction of cyclic or multicyclic structures and reduces the number of end group. (2) It prevents gelation. (3) It reduces the molecular weight. (4) It reduces the polydispersity. It is characteristic for all polycondensations in solution or in the melt that the extent of cyclization increases with higher conversions and lower concentrations. Particularly important for the proper understanding of all step-growth polymerizations is the "self-dilution" of the active species, which proceeds automatically with an increasing conversion, as expressed in eqs 3 and 4.

BIOGRAPHICAL INFORMATION

Hans Rytger Kricheldorf was born and educated in Germany. He obtained his diploma and Ph.D. in chemistry from the University of Freiburg im Breisgau. He continued his academic career in Freiburg im Breisgau, with the tenure (habilitation) in 1975, and

was appointed Associate Professor in 1980. In 1982, he took over a Full Professor position for polymer science at the University of Hamburg. His research activities concern two life-long working fields, namely, ring-opening polymerization and polycondensation. The preparative work mainly concerned biodegradable polymers, thermostable engineering plastics, and liquid-crystalline polymers. More recently, his research interests also focus on syntheses of cyclic and multicyclic polymers.

FOOTNOTES

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REFERENCES

1 Carothers, W. H. Polycondensation. *Chem. Rev.* **1931**, *8*, 353–428.

2 Flory, P. J. Fundamental principles of condensation polymerization. *Chem. Rev.* **1946**, 137–197.

3 Stanford, J. L.; Stepto, R. F. T.; Waywell, D. R. Rate theory of irreversible linear random polymerization, part 2. *J. Chem. Soc., Farraday Trans. 1* **1975**, *71*, 1308–1326.

4 Gordon, M.; Temple, W. Ring-chain competition kinetics in linear polymers. *Makromol. Chem.* **1972**, *152*, 277–289.

5 Roovers, J. In *Cyclic Polymers*; Semlyen, J. E., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; Chapter 10: Organic Cyclic Polymers, pp 347–384.

6 Ederle, Y.; Naneghi, K. S.; Lutz, P. J. Synthesis of cyclic macromolecules. In *Materials Science and Technology*, Schlüter, A. B., Ed.; Wiley VCH Publishing: Weinheim, Germany, 1999; Chapter 19, pp 621–647.

7 Tezuka, Y. Topological polymer chemistry: Classification and construction of non-linear polymer architectures. *Macromol. Symp.* **2003**, *192*, 217–226.

8 Tezuka, Y.; Tsuchitani, A.; Ocke, H. Synthesis of topological isomers through electrostatic self-assembly and covalent fixation with telechelic poly(TFH) having cyclic ammonium salt groups. *Polym. Int.* **2003**, *52*, 1579–1583.

9 Krichelord, H. R.; Schwarz, G. Cyclic polymers by kinetically-controlled step-growth polymerization. *Macromol. Rapid Commun.* **2003**, *24*, 359–381.

10 Kricheldorf, H. R.; Fan, S.-Ch. Cyclic polyimides—A comparison of synthetic methods. *High Perform. Polym.* **2004**, *16*, 543–555.

11 Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. Cyclic poly(pyridine ether)s by the polycondensation of 2,6-difluoropyridine with various diphenols. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4781–4789.

12 Kricheldorf, H. R.; Lomadze, N.; Fritsch, D.; Schwarz, G. Cyclic and telechelic ladder polymers derived from tetrahydroxytetramethyl-spirobisindane and 1,4-dicyanotetrafluorobenzene. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5344–5352.

13 Kricheldorf, H. R.; Böhme, S.; Schulz, C.-L. Cyclic polycarbonates by hydrolytic polycondensations of bisphenol-A bischloroformiate. *Macromol. Chem. Phys.* **2002**, *23*, 803–808.

14 Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Schultz, C. L. Cyclic polycarbonates by polycondensation of bisphenol-A with triphosgene. *Macromolecules* **2004**, *37*, 1742–1748.

15 Kricheldorf, H. R.; Al Masri, M.; Schwarz, G. Cyclic polyamide-6 by thermal polycondensation of ε-caprolactam and ε-aminocaproic acid. *Macromolecules* **2003**, *36*, 8648–8651.

16 Kricheldorf, H. R.; Zang, Q.-Z.; Schwarz, G. New polymer syntheses 6. Linear and branched poly(3-hydroxybenzoate)s. *Polymer* **1982**, *23*, 1821–1830.

17 Hawker, C. J.; Frechet, J. M. One-step synthesis of hyperbranched dendritic polyesters. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4586.

18 Turner, R. S.; Voit, B. I.; Mourey, T. All aromatic hyperbranched polyesters with phenol and acetate end groups. Synthesis and characterization. *Macromolecules* **1993**, *26*, 4617–4623.

19 Voit, B.; Turner, R. S. Dendritische und hyperbranched polymere. *Angew. Macromol. Chem.* **1994**, *223*, 13–27.

20 Moeck, A.; Burguth, A.; Hanselmann, R.; Frey, H. Synthesis of hyperbranched homo- and copolyesters via the slow monomer addition method. *Macromolecules* **2001**, *34*, 7692–7698.

21 Kricheldorf, H. R.; Bolender, O.; Wollheim, T. New polymer syntheses 103. In situ endgroup modification of hyperbranched poly(3,5-dihydroxybenzoate)s. *Macromolecules* **1999**, *32*, 3878–3882.

22 Kuchanov, S.; Slot, H.; Stocks, A. Development of a quantitative theory of polycondensations. *Prog. Polym. Sci.* **2004**, *29*, 563–635 (see p 615).

23 Erlander, S.; French, D. A. A statistical model for amylopectin and glycogen. The condensation of A—R—Bg$_{-1}$ units. *J. Polym. Sci.* **1956**, *20*, 7–28.

24 Allen, E. S. A probability theory for the condensation of A—R—B$_2$ units. *J. Polym. Sci.* **1956**, *21*, 349–350.

25 Galina, H.; Lechowicz, J. B.; Kaczmarski, K. Kinetic models of the polymerization of an ab$_2$ monomer. *Macromol. Theory Simul.* **2001**, *10*, 174.

26 Galina, J.; Lechowicz, J. B.; Walczak, M. Kinetic modelling of hyperbranched polymerization involving an ab$_2$ monomer reacting with substitution effect. *Macromolecules* **2002**, *35*, 3253–3260.

27 Holter, D.; Burgath, A.; Frey, H. Degree of branching in hyperbranched polymers. *Acta Polym.* **1997**, *48*, 30–35.

28 Holter, D.; Frey, H. Degree of branching (DB) in hyperbranched polymers. Part 2. Enhancement of the DB scope and limitation. *Acta Polym.* **1997**, *48*, 298–309.

29 Beginn, U.; Drohmann, C.; Möller, M. Conversion dependence of the branching density for the polycondensation of Ab$_n$ monomers. *Macromolecules* **1997**, *30*, 4112–4116.

30 Schmaljohann, D.; Barratt, J. G.; Komber, H.; Voit, B. Kinetics of non-ideal hyperbranched polymerizations. 1. Numeric modeling of the structural units and the diads. *Macromolecules* **2000**, *33*, 6284–6294.

31 Cheng, K. C.; Don, T. M.; Gao, W.; Chuang, T.-H. Kinetic model of hyperbranched polymers formed by the polymerization of ab$_2$ monomers with a substitution effects. *Polymer* **2002**, *43*, 6315–6322.

32 Dusek, K.; Smivarsky, J.; Smrekova, M.; Simonsik, W. J.; Wilczek, L. Role of cyclization in the degree of polymerization distribution of hyperbranched polymers. Modeling and experiments. *Polym. Bull.* **1999**, *42*, 489–496.

33 Kim, Y. H.; Webster, O. Hyperbranched polymers. *J. Macromol. Sci., Part C: Polym. Rev.* **2002**, *42*, 55–89.

34 Voit, B. New developments of hyperbranched polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505–2525.

35 Voit, B. Hyperbranched polymers. All problems solved after 15 years of research. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2679–2699.

36 McKee, M. G.; Unal, S.; Wilke, G. L.; Long, T. E. Branched polyesters: Recent advances in synthesis and performance. *Prog. Polym. Sci.* **2005**, *30*, 507–539.

37 Percec, V.; Chu, P.; Kawasumi, M. Toward willow-like thermotropic dendrimers. *Macromolecules* **1994**, *27*, 4441–4453.

38 Park, O.; Feast, W. J. Synthesis, structure and properties of hyperbranched polyesters based on dimethyl(2-hydroxyethoxy)isophthalate. *Macromolecules* **2001**, *34*, 2048–2059.

39 Martinez, C. A.; Hay, A. S. Preparation of hyperbranched macromolecules with aryl fluoride and phenol terminal functionalities using new monomers and C$_2$CO$_3$ or Mg(OH)$_2$ as the condensing agent. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2015–2019.

40 Burgath, A.; Sunder, H.; Frey, H. Role of cyclization in the synthesis of hyperbranched aliphatic polyesters. *Macromol. Chem. Phys.* **2000**, *201*, 782–791.

41 Sepulchre, M.; Sepulchre, M.-O.; Belleney, J. Aliphatic hyperbranched polyesters by polycondensation of potassium 2,5-bis(bromomethyl)benzoate: Formation of cyclic structures. *Macromol. Chem. Phys.* **2003**, *204*, 1679–1705.

42 Gooden, J. K.; Gross, M. C.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. Cyclization in hyperbranched polymer syntheses: Characterization by MALDI—TOF mass spectrometry. *J. Am. Chem. Soc.* **1998**, *120*, 10180–10186.

43 Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Krüger, R.-P. Cyclic hyperbranched poly(ether ketone)s from 3,5-bis(4-fluorobenzoyl)phenol. *Macromolecules* **2003**, *36*, 5551–5558.

44 Callahan, J. W. General Electric Co., U.S. Patent 1,108,329, 1914.

45 Kienle, K. H.; Hovey, A. G. The polyhydric alcohol—polybasic acid reaction I. Glycerol—phthalic anhydride. *J. Am. Chem. Soc.* **1929**, *51*, 509–519.

46 Kienle, K. H.; Petke, F. E. The polyhydric alcohol—polybasic acid reaction VI. The glyceryl adipate and glyceryl sebacate polyesters. *J. Am. Chem. Soc.* **1941**, *63*, 481–484.

47 Flory, P. J. Molecular size distribution in three-dimensional polymers. II. Trifunctional branching units. *J. Am. Chem. Soc.* **1941**, *63*, 3091–3096.

48 Colquhoun, H. M.; Arico, F.; Williams, D. J. One-step synthesis of very large cage-type molecules from aromatic subunits. *Chem. Commun.* **2001**, 2574–2575.

49 Colquhoun, H. M.; Arico, F.; Williams, D. J. Non-covalent dimerization of bicyclic aromatic oligomer via loop—loop interlocking in the solid state. *New J. Chem.* **2002**, *26*, 1703–1705.

50 Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. Multicyclic poly(ether sulfone)s of phloroglucinol forming branched and crosslinked architectures. *Macromolecules* **2003**, *36*, 4337–4344.

51 Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. Synthesis and functionalization of poly(ether sulfone)s based on 1,1,1-tris(4-hydroxyphenyl) ethane. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2967–2978.

52 Garaleh, M.; Polefka, C.; Schwarz, G.; Kricheldorf, H. R. Multicyclic poly(ether sulfone)s derived from 1,1,1-tris(4-hydroxyphenyl) ethane. *Macromol. Chem. Phys.* **2007**, *208*, 747–755.

53 Kricheldorf, H. R.; Hobzova, R.; Schwarz, G.; Vakhtangishvili, L. Multicyclic poly(benzonitrile ether)s based on 1,1,1-tris(4-hydroxyphenyl) ethane and isomeric difluorobenzonitriles. *Macromolecules* **2005**, *38*, 1736–1746.

54 Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Prosenc, M. Multicyclic polyethers with pendant keto groups by polycondensation of 1,1,1-tris(4-hydroxyphenyl) ethane. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6233–6246.

55 Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G. Multicyclic polyethers derived from 1,1,1-tris(4-hydroxyphenyl) ethane and 2,6-dihalopyridines. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5725–5735.

56 Kricheldorf, H. R.; Jahnke, P.; Scharnagl, N. New polymer syntheses 58. Alkylation of aromatic poly(pyridine ether)s and their application as membranes. *Macromolecules* **1992**, *25*, 1382–1386.

57 Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. Cyclic poly(pyridine ether)s by the polycondensation of 2,6-difluoropyridine with various diphenols. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *40*, 4781–4789.

58 Kricheldorf, H. R.; Hobzova, R.; Vakhtangishvili, L.; Schwarz, G. Multicyclic poly(ether ketone)s obtained by polycondensation of 2,6,4′-trifluorobenzophenone with various diphenols. *Macromolecules* **2005**, *38*, 4630–4637.

59 Kricheldorf, H. R.; Hobzova, R.; Vakhtangishvili, L.; Schwarz, G. Multicyclic poly(ether ketone)s by polycondensation of 1,3,5-tris(4-fluorobenzoyl) benzene with various diphenols. *Macromol. Chem. Phys.* **2005**, *206*, 2133–2142.

60 Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. Syntheses of polyethers from pentafluorobenzonitrile or pentafluorobenzophenone and flexible diphenols. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2007**, *4*, 783–788.

61 Kricheldorf, H. R.; Lomadze, N.; Polefka, C.; Schwarz, G. Multicyclic poly(ether ester)s by polycondensation of oligo(ethylene glycol)s and trimesoyl chloride. *Macromolecules* **2006**, *39*, 2107–2112.

62 Kricheldorf, H. R.; Bornhorst, K.; Schwarz, G. Multicyclic poly(ether ester)s by polycondensation of ethoxylated pentyerythritol with dicarboxylic acid dichlorides. *Macromol. Chem. Phys.* **2007**, *208*, 2463–2469.

63 Kricheldorf, H. R.; Bornhorst, K.; Schwarz, G. Multicyclic polythioesters derived from pentaerythritol tetramercaptoacetate. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*, 511–515.

64 Kricheldorf, H. R.; Bornhorst, K.; Schwarz, G. Multicyclic polyesters by polycondensation of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane with dicarboxylic acid dichlorides. *Macromolecules* **2007**, *40*, 199–204.

65 Kricheldorf, H. R.; Lomadze, N.; Schwarz, G. Multicyclic polyethers of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane and di- or triethylene glycol multipotent kryptands. *Macromolecules* **2007**, *40*, 4818–4822.

66 Kricheldorf, H. R.; Bornhorst, K. Cyclic and multicyclic poly(ether sulfone)s by polycondensation of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane with 4,4′-difluorodiphenyl sulfone. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5597–5605.

67 Kricheldorf, H. R.; Bornhorst, K. Syntheses of multicyclic poly(ether sulfone)s from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane and 4,4′-bis(4-chlorophenyl) sulfones. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3731–3739.

68 Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. Multicyclic polyethers derived from 1,4-dicyanotetrafluorobenzene and flexible diphenols. *Macromolecules* **2006**, *39*, 6445–6450.

69 Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. Multicyclic polyethers by the polycondensation of 1,2- or 1,3-dicyanotetrafluorobenzene with flexible diphenols. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5546–5556.

70 Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. Multicyclic polyethers derived from tetra(bromomethyl) methane and flexible diphenols. *Macromol. Chem. Phys.* **2006**, *207*, 1556–1563.

71 Kudo, H.; Hayashi, R.; Mitani, K.; Yokozawa, T.; Kasuga, N. C.; Nishikubo, T. Molecular waterwheel (Noria) from a simple condensation of resorcinol and an alkane diol. *Angew. Chem., Int. Ed.* **2006**, *45/47*, 7948–7952.

72 Kudo, H.; Shigematsu, K.; Mitani, K.; Nishikubo, T. One-pot synthesis of a nover ladder polymer of calixarene via condensation reaction of resorcinol and alkane diol based on dynamic covalent chemistry. *Macromolecules* **2008**, *41*, 2030–2036.

73 Kricheldorf, H. R.; Fechner, B. Polylactones 58. Star-shaped polylactones with functional endgroups via ring-expansion polymerization with a spiroinitiator. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1047–1057.

74 Kricheldorf, H. R.; Fechner, B. Biodegradable networks via ring-expansion polymerization of lactones and lactides with a spirocyclic tin initiator. *Biomacromolecules* **2002**, *3*, 691–695.

75 Mehrotra, R. G.; Chandra, G. Reactions of orthiesters of germanium Part II. Reactions of tetraethoxygermanium with glycols. *J. Chem. Soc.* **1963**, 2804–2806.

76 Kricheldorf, H. R.; Rost, S. Spirocycles versus networks-polycondensations of Ge(OEt)$_4$ with various aliphatic α,ω-diols. *Macromolecules* **2004**, *37*, 7955–7959.

77 Kricheldorf, H. R.; Rost, R. Spirocycles as stable alternative of networks—polycondensations of oligoether diols with metal tetraalkoxides. *Polymer* **2004**, *45*, 3205–3213.