Macrocycles. 21. Role of Ring−Ring Equilibria in Thermodynamically Controlled Polycondensations

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ABSTRACT: A new hypothesis is presented saying that an ideal thermodynamically controlled polycondensation is characterized by the following three aspects: first, the ring−chain equilibria automatically include ring−ring equilibria which become decisive for the thermodynamical properties of the system at high conversions. Second, at 100% conversion, all reaction products are cycles. Third, the chain growth is limited by the thermodynamical properties of the ring−ring equilibrium. The following polycondensations were discussed: base-catalyzed transesterification of ethyl cholate and combinations of $Bu_2Sn(OMe)_2$ with α,ω-poly(ethylene glycol)s, with poly(tetrahydrofuran)diols or with two oligosiloxane diols. Moreover, equilibrations of oligo- and polysiloxanes and polycondensations of Bu_2Sn bisacetate with various aliphatic dicarboxylic acids are discussed. Furthermore, polycondensations of pentaerythritol and its oligoether derivatives with $Bu_2Sn(OMe)_2$ yielding spirocycles are discussed. It is demonstrated by a variety of chemical or analytical methods that Sn-containing polymers were never formed and that cycles were the only reaction products. These results clearly support the above formulated modifications of the Jacobson−Stockmayer theory and of the Carothers−Flory theory.

Introduction

The classical theory of step growth polymerizations as it is present in all textbooks of polymer science is based on the work of Carothers[1] and Flory.[2,3] It assumes that linear monomers react with each other yielding linear oligomers and finally linear polymers. The growth of the average degree of polymerization ($\overline{DP}$) with the conversion (p) is assumed to follow the "Carothers equation" [1] (eq 1, with N_o and N_t as the number of

$$\overline{DP} = \frac{1}{1-p} \qquad (1)$$

$$p = \text{conversion: } \frac{N_o - N_t}{N_o}$$

functional groups at the starting point and at a later time) provided that no side reaction destroying functional groups occur and that the stoichiometry is perfect (the ideal case). No interference of cyclization reaction was taken into account for reasons explicitely discussed by Carothers[1] and Flory.[2] However, it was later observed that in many polycondensations cyclic oligomers were formed via "back-biting" reactions from active chains ends. This and other equilibration reactions have the consequence that the population of reaction products represents the thermodynamically defined energetic minimum of the system at any conversion, and thus, this type of polycondensation may be called "thermodynamically controlled polycondensations", TCPs.

In 1950 Jacobson and Stockmayer[4,5] have published two papers describing the molecular weight distribution of the cycles resulting from the ring−chain equilibria in TCPs. In the meantime, several research groups[6−13] have published experimental studies of such ring−chain equilibria and have confirmed that the Jacobson−Stockmayer theory (J.-S. theory) is in principle correct so far as formation and population of cyclic oligomers are concerned. To the best of our knowledge, we have not seen any comment that the J.-S. theory is in contradiction to the Carothers−Flory theory (C.-F. theory). Obviously, the J.-S. theory was and is understood as a modification and expansion of the C.-F. theory. This view is in good agreement with Flory's comments on the J.-S. theory. Flory has calculated[3] that a TCP of flexible monomers/polymers in bulk will result in 2.5 wt % of cycles, when the molar concentration of the monomers corresponds to 10 mol/L, higher or lower molar concentrations mean 2.0−3.0 wt % of cycles. Hence, 97−98 wt % of the entire reaction product is concentrated in one giant chain at quasi 100% conversion.

On this basis it is of interest to figure out what happens when a TCP is performed under ideal conditions (as defined above) to almost 100% conversion. According to the C.-F. theory, the final stage of any step growth polymerization is one giant polymer chain, and the J.-S. theory modifies this conclusion by saying that the chain ends of this giant polymer are in equilibrium with cyclic oligomers and polymers. Therefore, only a small weight fraction of cycles is present in a polycondensation conducted in bulk, whereas the fraction of cycles rapidly increases upon dilution due to a gain in entropy. This consistent interpretation of the C.-F. and J.-S. theory was summarized in Figure 2 of Jacobson and Stockmayer's publication in 1950 (reproduced as Figure 1 in this work). A slight modification of the J.-S. theory of ring−chain equilibria was later published by Flory, Suter, and Mutter.[14,15] Other authors[6] (most recently Ercolani et al.[8]) described further mathematical approaches to the problem of ring−chain equilibria. However, the question what happens when a TCP approaches 100% conversion was not discussed in all those publications.

The purpose of the present work was to examine and to discuss to what extent the combined C.-F. and J.-S. theories agree with real polycondensations and with our recently published[16,17] theory of kinetically controlled polycondensations (KCPs).

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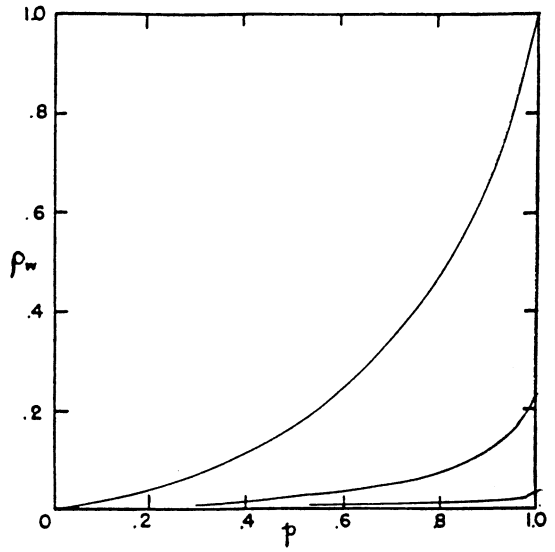


FIG. 2. Weight fraction of rings, ρ_w, as a function of the extent of reaction, p, for a Case IIIa polymer at three dilutions. Upper curve, $B'/c=0.5$; middle curve, $B'/c=0.05$; lower curve, $B'/c=0.005$.

Figure 1. Original Figure 2 and legend as published in ref 4 (lower B'/c values mean higher concentrations). (Reprinted with permission from ref 4. Copyright 1950 American Institute of Physics.)

Results and Discussion

The Hypothesis. In previous publications[16−19] dealing with the role of cyclization in kinetically controlled polycondensations (KCP) the following results were obtained. First, on the basis of MALDI−TOF mass spectra allowing the detection of individual polymers up to masses around 50 000 Da, it was found that cyclization competes with propagation at any stage of the polycondensation and at any concentration. Second, any optimization of the reaction conditions favoring higher molecular weights automatically enhanced the formation of cycles. Third, these results agree with the calculations of Stepto et al.[20,21] and Gordon et al.[22] who postulated that an ideal KCP yields 100% cycles of any size at 100% conversion.

These results suggest the following consequences for the theory of ideal TCPs. First, cyclizations involving both chain ends of reactive oligomers or polymers occur at any stage of the polymerization. Because of the "back-biting" reactions the molar ratio of small cycles vs large cycles will be higher than in the case of KCPs in agreement with calculations of Jacobson and Stockmayer.[4,5] Second, since "back-biting" does not prevent cyclization via both chain ends, all reaction products will be cycles at 100% conversion. Latest at this point the reaction mixture needs to be described as ring−ring equilibrium. Third, the thermodynamics of the ring−ring equilibrium limits the chain growth. The ring−ring equilibrium depends very much on the cyclization tendency of individual monomers/polymers which is an inherent property of their structure. In this respect the present hypothesis is in conflict with the predictions of the Carothers equation. Furthermore, the ring−ring equilibrium is concentration and temperature dependent, because lower concentrations and higher temperatures favor the formation of smaller (strain-free) macrocycles at the expense of larger ones due to a gain in entropy. Therefore, both concentration and temperature have an influence on the maximum molecular weight which can be achieved in an ideal TCP.

In this context, we have to discuss which role cyclizations play in real polycondensations, which will never be ideal and not reach exactly 100% conversion due to side reactions. At this point, it is important to take into account that by definition a TCP involves an equilibration of all components of the reaction mixture. Hence, a TCP may be considered as a combination of chain−chain, ring−chain, and ring−ring equilibria. To simplify the mathematical treatment of the ring-size distribution and its correlation with conformational properties, Jacobson and Stockmayer have focused their work on ring−chain equilibria. This simplification is not satisfactory for a proper understanding of the entire course of a TCP up to 100% conversion. With higher and higher conversion the average length of all chains increases and the total number of molecules decreases. However, the molar ratio of cycles vs linear chains will systematically increase, because long chains can produce large cycles in addition to the small ones, whereas the short chains cannot. In this way, the reaction mixture gradually approaches the final state with 100% cycles at 100% conversion. This scenario has the consequence that at a certain point of the conversion the reaction mixture contains more cycles than linear species. From this point on the thermodynamical properties of the reaction mixture are dominated by the ring−ring equilibria. At even higher conversion an ideal TCP may be considered as a ring producing process with the linear chains playing the role of a catalyst of the ring−ring equilibria (eq 2). In this connection, it should be mentioned that

$$c(M)_x + c(M)_y \overset{\text{Cat}}{\rightleftharpoons} c(M)_{x+y} \qquad (2)$$

ring−ring equilibria may be obtained even in the absence of active polymer chains or catalysts as discussed below for cyclic tin alkoxides (or in the case of cyclic oligoamides and lactams). Therefore, it is not correct to describe a TCP at a high conversion exclusively in terms of ring−chain equilibria. This hypothesis disagrees with the C.-F. theory and with the J.-S. theory, which postulate one giant polymer chain (containing 97−98 wt % of the reaction product) as the main product at 100% conversion. The assumption of one giant polymer chain as endproduct of a polycondensation is unproven. It is nothing but a historic prejudice going back to the days of Carothers work,[1] when cyclization of long chains was considered to be almost impossible. This view needs to be changed as discussed in ref 20 and in the literature cited therein.

Finally, the question needs to be discussed why Jacobson and Stockmayer in their calculations of ring concentrations presented in Figure 1 (of this work) did not consider the formation of 100% cycles at 100% conversion for polycondensations performed in concentrated solutions or in bulk. Jacobson and Stockmayer calculated ring−chain equilibria for different solutions having different concentrations of reactants, and for each solution the molar concentration of the active species was kept constant regardless of the conversion. However, all step-growth polymerizations are self-diluting systems in terms of molarity of the linear active chains. The molar concentration of active species (e.g., monomers in the very beginning) decreases according to eq 3. At 100% conversion the concentration of active

$$[La]_p = [La]_0(1 - p) \quad (3)$$

$[La]_0$: initial molar concentration of active species (e.g., monomers at $p = 0$)

$[La]_p$: molar concentration of linear active species at a given conversion (including monomers)

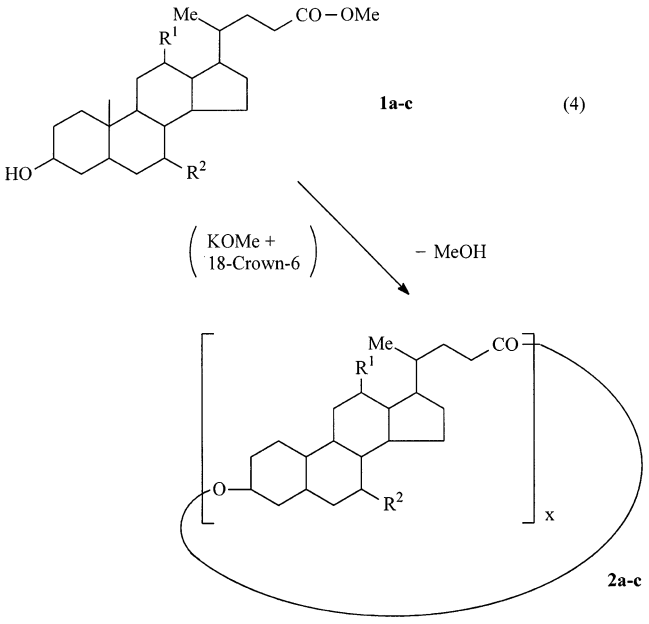
species is zero, and all reaction products are necessarily cycles. In summary, both kinetically and thermodynamically controlled polycondensations have in common, that they tend to yield exclusively cycles under ideal reaction conditions. Since the concentration plays a key role in the J.-S. theory, it is worthwhile to present two citations to underline the difference between the conclusions of Jacobson and Stockmayer, on one hand, and the present hypothesis, on the other:

"... there is a critical concentration below which the condensing system can be converted entirely into rings, but above which it is not possible" (p 1601 in ref 4).

"For $p = 1$, the ring fraction by weight increases linearly with B'/c, i.e., with dilution, until B'/c reaches 0.19, above which the equilibrium situation is 100% rings. The critical dilution, beyond which a system composed wholly of rings results, resembles the Bose–Einstein condensation phenomena" (p 1605 in ref 4).

These comments are the verbal equivalents of the original Figure 2 (i.e., Figure 1 in this work). In this connection, a fundamental property of all chemical reaction equilibria (in a homogeneous phase) should be considered: no component of an equilibrium can completely disappear (or appear from nowhere) just by variation of the concentration. By dilution of a ring–chain equilibrium, the length of the linear chains will decrease with increasing number of cycles but the number of linear species (including linear monomers) will not change when the conversion is kept constant. The only experimental factor which influences the number of linear species is the conversion, and with 100% conversion ($p = 1$) all linear species will disappear, regardless of the initial concentration (eq 3). In other words, a critical concentration responsible for the appearance or disappearance of linear species does not exist in TCPs. The only kind of limiting concentrations which plays a role in TCPs is the upper limit of active linear species which is given by eq 3 for step growth polymerizations performed in bulk (including the simplification that the volume of the reaction mixture remains constant during the step growth polymerization).

Polyesters. Several research groups[5,8,10–13,23,24] have studied ring–chain equilibria of polyesters beginning with Stockmayer and co-workers.[5] All these studies concentrated on the frequency distribution of the cyclic oligoesters, whereas the role of the conversion or the molecular weights of the linear polyesters involved in these equilibrations have not been considered. However, the work of Brady et al.[23] is remarkable for the following reason. Those authors studied the polycondensation of the methyl cholates **1a–c** (eq 4) and found a certain equilibrium distribution of cyclic oligoesters (**2a–c**) but no high molecular weight polyesters. They also isolated individual cyclic oligoesters and equilibrated them with the same transesterification catalyst (potassium methoxide), but again no high molecular weight polyester was found and the frequency distribution of the cycles was the same as that of the polycondensation experiment.



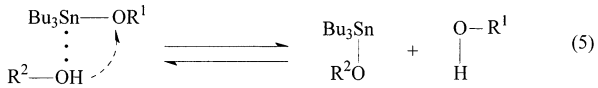
a: $R^1 = OCH_2C_6H_4C_6H_5$, $R^2 = H$

b: $R^1 = OCH_2C_6H_5$, $R^2 = OCH_2OCH_2CH_2OMe$

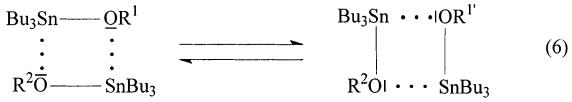
c: $R^1 = OCH_2C_6H_4OMe$, $R^2 = OCH_2C_6H_4OMe$

In this context, it should be mentioned that an equilibration of cyclic monomers or oligomers (typically involving ring-opening polymerization) is adequate to a TCP with almost 100% conversion. Hence, a TCP can be simulated by an equilibration of cycles, whereas an analogous simulation does not exist in the case of kinetically controlled polycondensations.

Polyethers. For a proper understanding of the polycondensations discussed below a short comment on a couple of fundamental properties of tin alkoxides may be useful. Tin alkoxides (regardless of Sn(II) or Sn(IV) compounds) can easily exchange alkoxide group with alcohols (or water) as outlined in eq 5.[25,26] Furthermore,



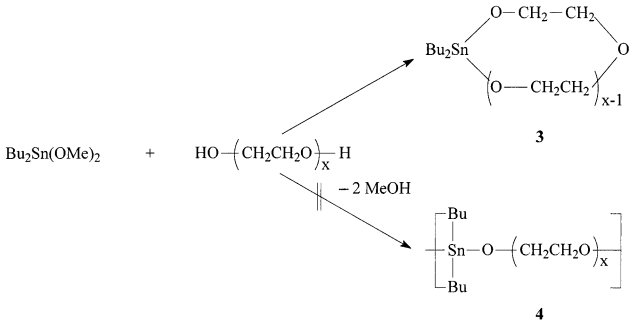
tin alkoxides can exchange alkoxide groups with each other (eq 6). Depending on the steric elements of the



substituents, this exchange may even occur below room temperature.[26] All these exchange and equilibration reactions have in common that an O atom of the reaction partner coordinates with Sn atom via free d or sp^3d^2 orbitals, thereby lowering the energy of activation of the exchange step. Therefore, the chemistry of Sn–O compounds is particularly suited for studies of equilibration reactions at moderate temperatures.

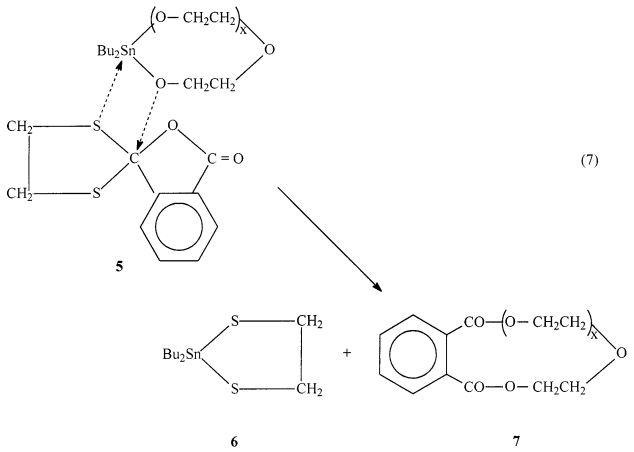
In two previous publications, we have reported on polycondensations of $Bu_2Sn(OMe)_2$ with oligo(ethylene oxide), PEOs,[27] or with poly(tetramethylene oxide) diols, PTMOs.[28] In the case of PEOs, five monodisperse oligomers were used [di- through hexa(ethylene glycol)]

Scheme 1



along with five polydisperse PEOs (up to PEO-2000). These "polycondensations" liberate methanol (Scheme 1) and thus, are equilibration reactions. The removal of the methanol by distillation (checked by ^{1}H NMR spectroscopy) shifts the equilibrium to the side of stannylenated PEOs (**3**). Regardless which PEO was used, polymers of structure **4** were never obtained. The solution viscosities of the condensation products were almost identical with those of the PEOs used as starting materials. The only reasonable explanation of these results is the conclusion that the reaction products **3** all have a cyclic structure. In addition to cycles containing one Bu_2Sn group (called here generation one), smaller amounts of larger cycles containing two Bu_2Sn groups (generation two) and more Bu_2Sn groups should be formed in an equilibrium. The formation of these higher molecular weights compensates for the shrinking of the volume due to cyclization, so that the viscosity values do not decrease. Unfortunately, the hydrolytic sensitivity of the Sn−O groups prevented a direct identification of these cycles by "fast-atom-bombardment" or "MALDI−TOF" mass spectrometry. The mass spectra display the peaks of the linear polyether diols resulting from the hydrolysis (or alcoholysis) of the Sn−O bonds.

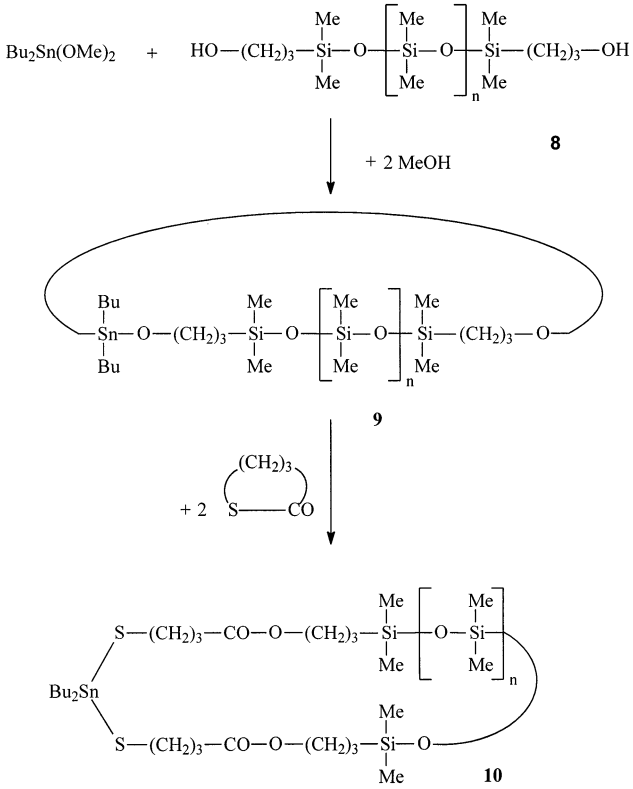
The existence of reactive Sn−alkoxide groups in these cycles was proven by quantitative reactions with lactones.[27,28] Furthermore, it has recently been found[29] that the cyclic stannylenated PEOs react almost quantitatively with the spirophthalide **5**. The insertion of this bicycle into an Sn−O bond is followed by extrusion of the 2-stanna-1,3-dithiolane **7** combined with the formation of the cyclic PEO phthalates **8** (eq 7). This reaction



(7)

sequence does not cause any ring cleavage and, therefore, proves the cyclic nature of the stannylenated PEOs used as starting materials.

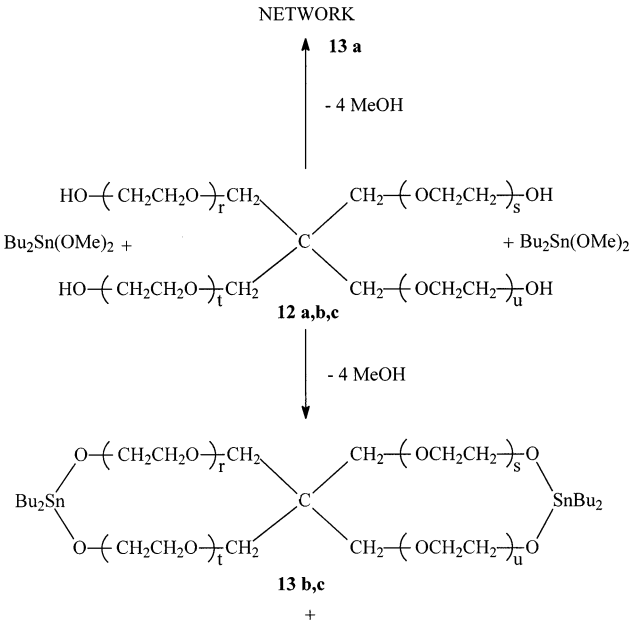
Scheme 2



Polysiloxanes. The hydrolysis of dichlorodimethylsilane yields dihydroxydimethylsilane which is unstable and easily undergoes polycondensation with elimination of water and formation of cyclic oligosiloxanes as the main reaction products.[30] Numerous research groups have studied the equilibration of isolated cyclic oligosiloxanes.[6,10,31,32] Most studies were concerned with the anionic equilibration in concentrated solutions (220−250 g/L) at moderate temperature (≤110 °C). Around 95 wt % of these equilibrates were identified as cycles (ref 10, p 28), far more than predicted by the J.-S. theory, even when the dilution by a factor of 4 relative to neat cyclosiloxanes is taken into account (in Figure 1, the concentration varies by a factor of 10 between the individual curves). Furthermore, the equilibration of cyclic siloxanes was studied in bulk at 390 °C and the expected bi- or trimodal SEC elution curves were obtained.[32] It was not clarified, if the high molecular weight fraction contained cycles. Yet, even when only the fraction of clearly identified cyclic oligomers and low polymers was taken into account, it amounted to 60−90 wt % far more than the 2.5 wt % expected for the polycondensation of the hypothetical monomer dihydroxydimethylsilane.

Quite recently, another kind of equilibration experiments was performed, using γ-hydroxypropyl-terminated polysiloxanes with M_ns of 1000 and 4000 g/mol as starting materials. These diols were polycondensed with $Bu_2Sn(OMe)_2$ and an almost quantitative liberation of methanol was confirmed by ^{1}H NMR spectroscopy (Scheme 2). However, the solution viscosities of the resulting "polycondensates" **9** were only slightly higher than those of the original polysiloxanes or their bisacetates. Therefore, these results exactly parallel the above-discussed "polycondensations" of poly(ether diol)s with $Bu_2Sn(OMe)_2$ (Scheme 1). The virgin reaction mixture obtained from the poly(siloxane) diol of M_n 1000

Scheme 3

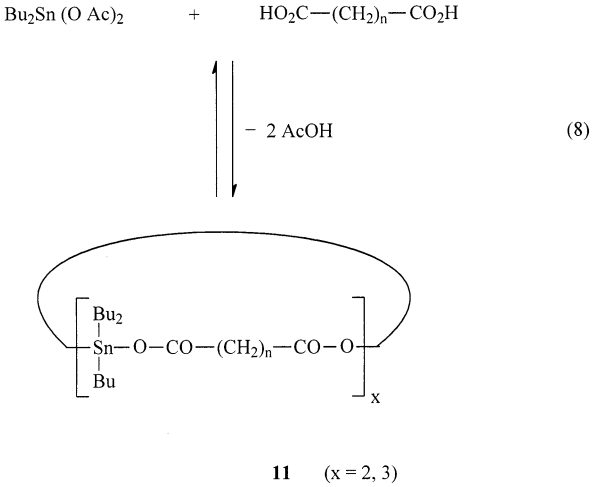


12 a: r + s + t + u = 0
12 b: r + s + t + u = 3
12 c: r + s + t + u = 15

Scheme 3

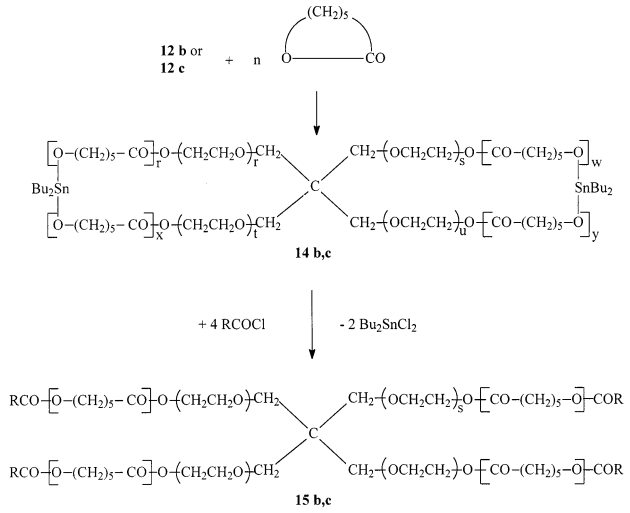
g/mol was in situ reacted with γ-thiobutyrolactone to obtain cycles insensitive to hydrolysis or alcoholysis under neutral conditions. The structure of these reaction products (i.e., structure **10**) was characterized by ^{1}H and ^{13}C NMR spectroscopy and by MALDI−TOF mass spectroscopy.[33] All results together confirmed that the polycondensations outlined in Scheme 3 yielded ring−ring equilibria. Therefore, these results perfectly agree with the equilibration of cyclosiloxanes and polysiloxanes reported in the literature.[30−32]

Poly(dibutyltin dicarboxylate)s. When dibutyltin bisacetate ($Bu_2Sn(OAc)_2$) is heated with aliphatic α,ω-dicarboxylic acids, acetic anhydride is liberated in an equilibration reaction (eq 8).[34,35] Removal of the acetic



anhydride in vacuo shifts the equilibrium to the side of the Bu_2Sn dicarboxylates. Dicarboxylic acids containing up to 22 carbon atoms were used for these experiments, but polymers were never obtained. Furthermore, three different synthetic methods were explored and compared. All synthetic methods yielded the same reaction products in agreement with a thermodynamic control of all syntheses. Viscosity measurements, vapor pressure osmometry, and MALDI−TOF measurements confirmed that the crystalline reaction products consisted of cyclic oligomers with a predominance of cyclic trimers.

Scheme 4



Spirocyclic Oligoethers vs Networks. Polycondensations of "a−a" with "b_3" or "b_4" type monomers offer an useful system to illustrate and to check the difference between the J.-S. theory and the concept of ring−ring equilibria. If a mixture of two "a−a" monomers and one "b_4" monomer (i.e., an equivalent mixture) is polycondensed in bulk or in concentrated solution up to 100% conversion, a gel containing more than 95% of the entire mass will necessarily be formed according to the J.-S. and to Flory theories. According to the hypothesis of this work, the situation of the ring−ring equilibrium will decide to what extent a gel or a mixture of spirocycles will be obtained. If the monomeric and dimeric spirocycles are strain-free, the equilibrium will be shifted to the side of the spirocycles and the network is thermodynamically unstable, because the formation of many spirocycles represents a tremendous gain in entropy. When the monomeric and oligomeric spirocycles possess ring strain, the ring−ring equilibrium is shifted to the side of high molecular weight products with the formation of gels.

In two recent publications, polycondensations of pentaerythritol (**12a**)[36,37] or ethoxylated pentaerythritols (**12b** and **12c**) with dibutyltin dimethoxide were described. With pentaerythritol (**12a**), an infusible mass insoluble in all inert solvents was obtained. Obviously, a gel was formed (**13a**) due to strain in the six-membered rings of the monomeric and oligomeric cycles (Scheme 3). The reaction products of the ethoxylated pentaerythritols (**13b** and **13c**) were completely soluble in various inert solvents. Their solution viscosities were low indicating the absence of gel particles (Scheme 3). These spirocycles reacted with lactones at four Sn−O bonds yielding larger spirocycles **14b** and **14c**, which were again strain-free and never did form gels (**15b** and **15c**, Scheme 4). The reaction with various carboxylic and chlorides yielded four-armed stars having functional end groups (Scheme 4). This reaction sequence provides additional evidence for the formation of the spirocycles **13b** and **13c** (plus higher oligomers). The formation of soluble spirocycles **13b** and **13c** and their quantitative

reactions with lactones was confirmed by another research group.[38]

Discussion

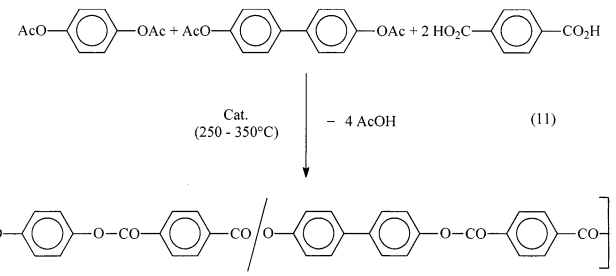
The results presented above clearly support the initially formulated hypothesis. Thermodynamically controlled polycondensations tend to end up with ring−ring equilibria and not with the formation of one giant chain in equilibrium with a few cycles. Since the formation of 100% cycles requires 100% conversion and absence of side reactions, it is, of course, difficult to achieve an absolute quantitative formation of cycles in a real experiment. However, the cited reaction products certainly contain more than 95 wt % of cycles in some cases (e.g., spirocycles) even around 99 wt %. These results have to be compared with the 2.5 wt % of circular reaction products predicted by Flory[3] for the J.-S. theory. Furthermore, no indication was found for a substantial fraction of linear chains having high molar masses (number-average molecular weights, M_ns, above 10^5 Da). Moreover, neither Stockmayer nor Flory have ever presented any experimental evidence for the J.-S. theory of TCPs. Results for TCPs performed in bulk yielding ≥95 wt % of the reaction product in the form of one (or two) giant chain(s) with M_ns > 10^6 Da and a polydispersity of 1.0 have never been published. Therefore, the ring−ring equilibrium hypothesis presented in this work is better substantiated by theoretical considerations and experimental results than the J.-S. theory.

This interpretation has the consequence that the chain growth of TCPs is in almost all cases limited by the thermodynamic properties of the ring−ring equilibria. This conclusion is summarized by eq 9, where K_c

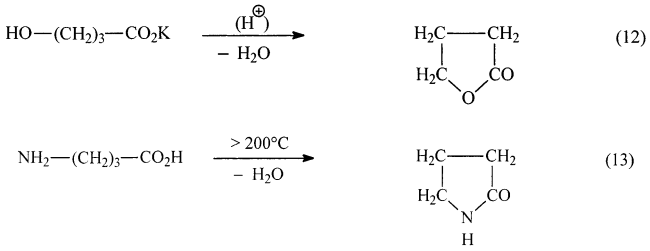
$$\overline{DP} = \frac{1}{1 - p(1 - 1/X^{K_c})} \tag{9}$$

with $$K_c = \frac{[c(M)_{x+y}]}{[c(M)_x][c(M)_y]} \quad \text{(see eq 2)} \tag{10}$$

is the ring−ring equilibrium constant as defined by eqs 2 and 10 and X is a factor >1 which allows a fitting of this equation to individual experiments including variation of the concentration. Equation 9 is a modification of the classical Carothers equation, eq 1, taking into account the influence of ring−ring equilibria (eqs 1, 2, and 9). It is, of course, a simplification to use a single equilibrium constant. At least for smaller cycles (e.g., < DP 20) a series of slightly different equilibrium constants has to be taken into account. However, the simplified eq 9 is useful to illustrate how real TCPs deviate from the classical C.-F. and J.-S. theories. Equation 9 indicates that the "Carothers equation" (1) is an extreme (or limiting) case characterized by the absence of cyclization ($K_c \rightarrow \infty$). Concrete experiments approaching this extreme are syntheses of "rigid-rod type" polyesters from parafunctionalized aromatic monomers by a method involving transesterification as examplified in eq 11. Syntheses of commercial liquid-crystalline polyesters such as "Vectra" or "Xydar" ("Sumicasuper") meet these requirements. However, a second extreme and limiting case needs to be considered for a complete description of TCPs, and this is the case where $K_c \rightarrow 0$. In this case a potential monomer will form thermodynamically stable cycles without propagation. Typical examples of thermodynamically controlled cyclizations are the formation of γ-butyrolactone from

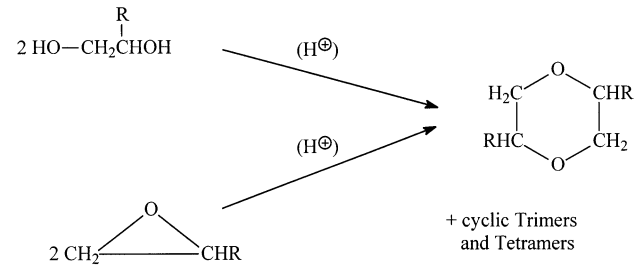


γ-hydroxybutyric acid (eq 12) or the formation of γ-butyrolactam from γ-aminobutyric acid (eq 13) at elevated



temperatures.[17] In these cases neither significant amounts of polymers nor of linear oligomers are formed. Another example of this kind is the acid-catalyzed condensations of 1,2-dihydroxyalkanes (or epoxides), which yield almost quantitatively 1,4-dioxanes in combination with a few cyclic oligomers[39] but no poly(ethylene glycol)s (Scheme 5).

Scheme 5



Most TCPs take a course between these extremes as illustrated by curves B−D in Figure 2. All these curves have in common that they hit the ordinate, which means the maximum DP that can be achieved under ideal conditions is limited by the ring−ring equilibrium. In real polycondensations the DPs will, of course, be lower, due to side reactions, imperfect stoichiometries, and incomplete conversions.

Conclusion

A hypothesis is formulated and discussed which assumes that the thermodynamical properties of TCPs are dominated at high conversions by ring−ring equilibria. A clean polycondensation conducted up to 100% will exclusively yield cycles as stable end products, regardless of the initial concentration. Thus, ring−ring equilibria determine the maximum $\overline{DP}$ that can be achieved under ideal reaction conditions. Depending on the ring−ring equilibria, either high molar mass rigid polymers or low molar mass cycles may be the main reaction products. The experimental results presented in this work by citation of pertinent literature data confirm this hypothesis. Together with the recently published concept of kinetically controlled polycondensations,[16−18] we have now a consistent theory for all

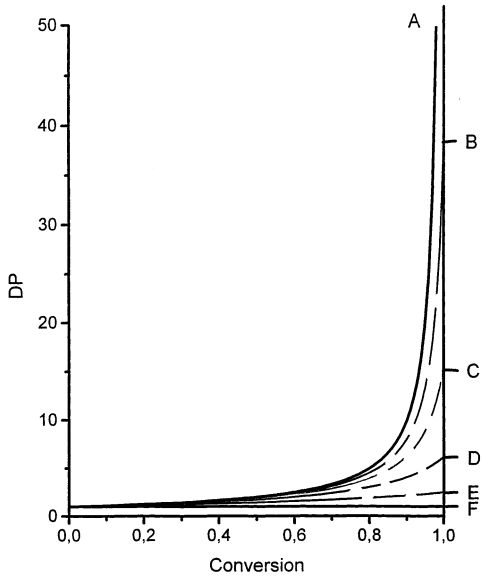


Figure 2. Graphic illustration of eq 9 calculated with $X = 1.2$: (A) $K_c = \infty$; (B) $K_c = 20$; (C) $K_c = 15$; (D) $K_c = 0.1$; (E) $K_c = 0$; (F) $K_c = 0$.

step-growth polymerizations, which can be summarized in eq 14 and in the following statement:

$$\overline{DP} = \frac{1}{1 - p(1 - 1/X^{\alpha})} \qquad (14)$$

$\alpha = K_c$ for thermodynamic control (TCPs)

$\alpha = V_p/V_c$ for kinetic control (KCPs)

V_p/V_c = rates of propagation and cyclization

"All step-growth polymerizations possess the fundamental tendency to yield cycles as stable endproducts with linear chains being the reactive intermediates or endproducts of side reactions."

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