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The Role of Ring-Ring Equilibria in Thermodynamically Controlled Polycondensations

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Summary: Thermodynamically controlled polycondensations (TCPs) involve rapid equilibration reactions, such as transesterification, transamidation, etc. An important component of these equilibration reactions is the reversible formation of cyclic oligomers and polymers by "back-biting". Therefore, TCPs were described in the previous literature in terms of ring-chain equilibria. The present study presents a complementary theory saying that ring-chain equilibria automatically include ring-ring equilibria which gain in importance with higher conversions because the molar ratio of rings versus linear chains rapidly increases. At 100% conversion, all reaction products will be cycles and the ring-ring equilibria limit the chain growth. Several polycondensations cited from the literature are discussed in the light of the new theory.

Keywords: back-biting, cyclic polymers, equilibration, polycondensation, ring-chain equilibrium

Introduction

In the classical theory of step-growth polymerizations elaborated by Carothers[1] and Flory[2,3] no differentiation was made between kinetically controlled polycondensations (KCPs) and thermodynamically controlled ones (TCPs). Characteristic for TCPs are rapid equilibration reactions (e.g. transesterification or transamidation) and Stockmayer and coworkers proved the reversible formation of cyclic oligomers and polymers via "back-biting".[4,5] As a consequence of the Jacobson-Stockmayer (J.S.) theory TCPs were exclusively described in terms of ring-chain equilibria.[6,7] This J.S. theory was and is understood as a modification of the Carothers-Flory (C.F.) theory which predicts on the basis of equation (1) that an ideal polycondensation reaching 100% conversion will yield one giant chain containing all monomeric units. Modification with the J.S. theory means that the giant chain obtained at

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100% conversion is at one or both ends in equilibrium with cyclic oligomers. The purpose of the present study is to propose and to discuss an alternative hypothesis saying that a proper understanding of TCPs requires a description in terms of ring-ring equilibria.

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

$\overline{DP}$ = average degree of polymerization

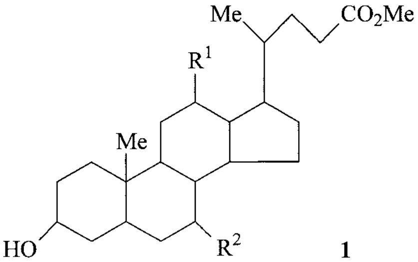
p = conversion

Results and Discussion

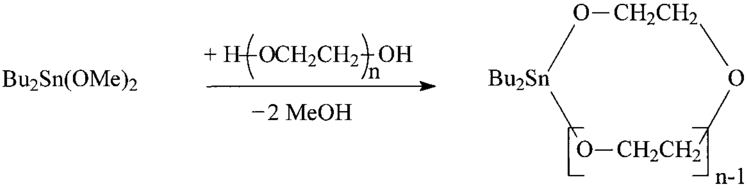
Experimental Results

On the basis of the J.-S. theory Flory has calculated[3] that a TCP conducted in bulk will contain around 2.5 weight% of cycles and one giant chain representing 97.5 weight% of the entire reaction product. In this article several previously published polycondensations should be cited which demonstrate that the reaction products do not contain a giant chain with 97-98 weight% of the entire mass, but mainly consist of cycles. In this connection, it should be mentioned that the final equilibrium of a TCP at 100% conversion does not depend on the reaction pathway, because no chemical equilibrium depends on the synthetic method and its kinetic implication. Therefore, an equilibration of monomeric or oligomeric cycles with a small amount of a catalyst (or without) is equivalent to a polycondensation with 100% conversion.

Recently, Brady et al.[8] studied the polycondensation of methyl esters of cholic acid derivatives (**1**) using solubilized potassium methoxide as transesterification catalyst. Those authors found an equilibrium of cyclic oligoesters free of high molecular weight linear polymers. Furthermore, a cyclic oligoester was isolated by HPLC and equilibrated with potassium methoxide. The same ring-ring equilibrium as that resulting from the polycondensation of **1** was obtained.



1

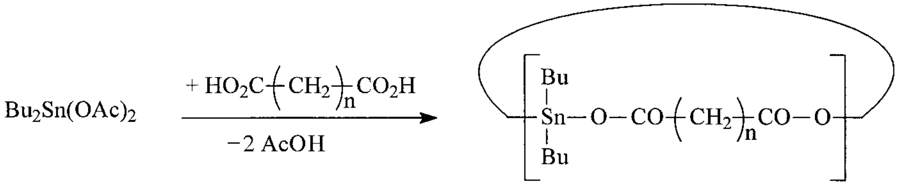


2

Polycondensations of dibutyltin dimethoxide with various monodisperse and polydisperse oligo- or poly(ethylene glycol)s were conducted by Kricheldorf and Langanke.[9] Regardless of the chain length of the diol mixtures, cyclic oligoethers (**2**) were isolated and no high molecular weight polyethers. Analogous results were obtained with poly(tetrahydrofuran)diols.[10] The equilibration of tin-alkoxide groups in these systems does not require a catalyst, because the exchange of alkoxide groups proceeds via O→Sn donor-acceptor interactions, even at room temperature.[11] The cyclic structure of tin-alkoxides, such as **2**, is proven by a variety of reactions and measurements,[12,13] but the sensitivity of the Sn-O bond to hydrolysis and alcoholysis prevents the direct characterization by "fast atom bombardment" or MALDI-TOF mass spectrometry.

Exclusively cyclic oligomers and no high molecular weight species (**3**) were isolated from polycondensations of dibutyltin bisacetate with various aliphatic dicarboxylic acids.[14]

Three different synthetic methods were compared which all yielded the same thermodynamically controlled reaction products.



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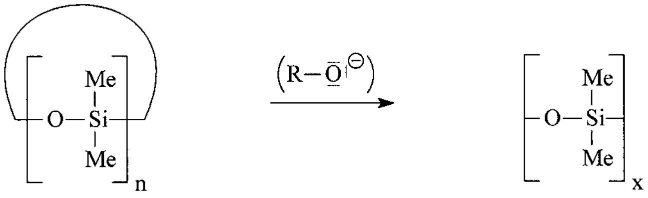
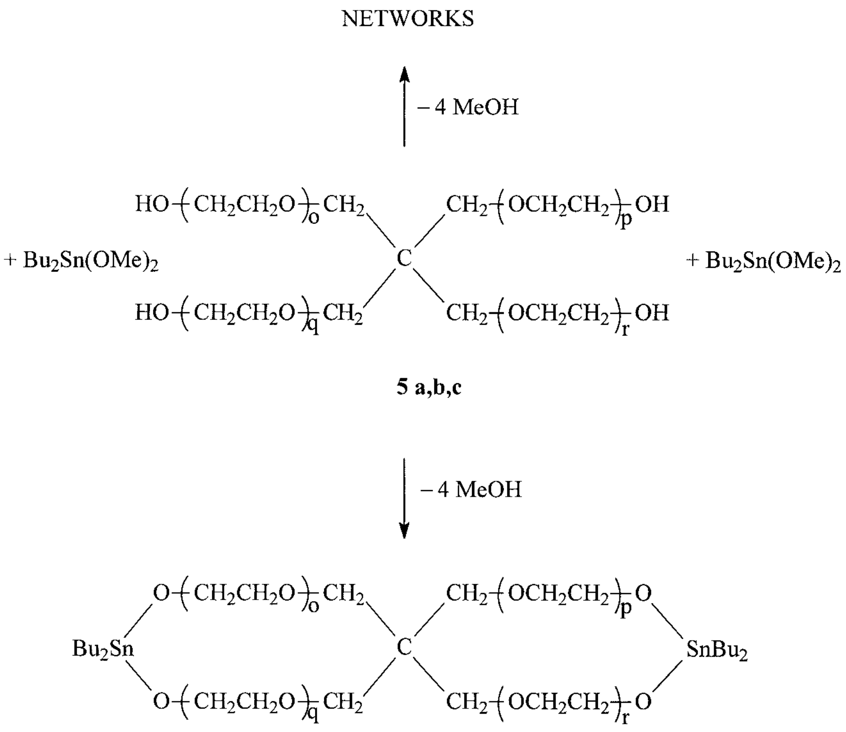


4

The equilibration of cyclosiloxanes in concentrated solution (23-24 weight%) or in bulk was studied by numerous authors.[6,15-17] All these studies were performed at a time when MALDI-TOF mass spectrometry was not available, so that the characterization of the small fraction of high molecular weight polysiloxanes was not feasible in those studies. However, the high fraction of clearly identified cyclosiloxanes (70-95 weight%) found in all studies is in contradiction to the small percentage expected from the J.S. theory.[3]

Finally, polycondensations of dibutyltin dimethoxide with penthaerythritol (**5a**) and ethoxylated derivatives (**5b,c**) should be mentioned.[18-20] According to the J.-S. and C.-F. theories, networks should be formed above 65% conversion. An infusible and insoluble gel was indeed obtained from **5a**, obviously because the 6-membered rings of the hypothetical spirocyclic oligomers **6a** possess ring strain. This ring chain shifts the ring-ring equilibrium to high molecular weight polymers which, in this case, are necessarily networks. However, the ethoxylated derivatives **5b** and **5c** yielded strain-free spirocycles (**6b** + **6c** and higher oligomers). At this point it should be mentioned that aliphatic ethers favor gauche conformations (in contrast to alkane chains) which, in turn, favor the formation of loops and larger cycles. The ring-ring equilibrium is then shifted to the side of the spirocycles, because the degradation of a gel to spirocycles includes a high gain in entropy.



5 a,b,c

6 a,b,c
(+ higher oligomers)

a: $o + p + q + r = 0$

b: $o + p + q + r = 3$

c: $o + p + q + r = 15$

Discussion

The experiments presented above have in common that the reaction products were mixtures of cyclic oligomers and polymers and a significant fraction of high molecular weight linear polymers was not detectable. Hence, these results are in contradiction to the J.S. and C.F. theories, but agree with our theory of ring-ring equilibria.

Any TCP involves three kinds of equilibria: the chain-chain, the ring-chain and the ring-ring equilibrium because all components of a reaction mixture are engaged in the equilibration process. A description of TCPs exclusively in terms of a ring-chain equilibrium is a simplification which is helpful to simplify the mathematical treatment, but it is misleading when the consequences of high conversions are considered. The molar concentration of linear active species (including monomers) rapidly decreases with higher conversions as formulated in equation (2). Therefore, the molar ratio of cycles versus linear molecules permanently increases and all reaction products are necessarily cycles at 100% conversion. The assumption that 100% conversion yields one giant chain is a contradiction in itself, which was born at the time of Carothers when cyclization of long chains was considered to be almost impossible.[1,2] However, in connection with studies of KCPs, we have recently demonstrated[21] that polycarbonates with a DP of 200 easily cyclize and this DP corresponds to a DP of 10^3 for polyolefins. Further improvements of the mass spectrometry will certainly expand the limits for the identification of cyclic polymers to still higher masses.

$$[\mathrm{La}]_p = [\mathrm{La}]_o(1-p) \qquad (2)$$

La = linear active species including monomers

$$c(M)_x + c(M)_y \overset{K_C}{\rightleftharpoons} c(M)_{x+y} \qquad (3)$$

$$\overline{DP} = \frac{1}{1-p(1-X^{-K_c})} \qquad (4)$$

When with increasing conversion the cycles begin to outnumber the linear species, a TCP may be described as a ring-ring equilibrium, because the chain-chain and ring-chain equilibria lose influence on the thermodynamical properties of the system. The final state of a TCP at 100% conversion is a neat ring-ring equilibrium which allows a schematic formulation by equation (3). The assumption of one single equilibrium constant (K_c) is, of course, a simplification, but it facilitates to illustrate the influence of ring-ring equilibria on the chain growth in a TCP. This influence is formulated in equation (4). The chain growth of an ideal TCP is limited by the ring-ring equilibrium, but in the case of rigid chains with high K_c values, equation (4) approaches the classical "Carothers equation" (1).

On the other hand, K_c values close to 0 indicate an almost complete formation of strain-free monomeric cycles as it is known from polycondensations of γ-hydroxy- or γ-aminobutyric acid which yield the thermodynamically stable γ-butyrolactone or γ-butyrolactam in nearly 100% yield. This short discussion demonstrates that the theory of ring-ring equilibria covers the full range of thermodynamically controlled cyclizations and polycondensations known from organic and macromolecular chemistry.

Finally, it should be discussed, why the fraction of cycles in technical TCPs are relatively low. Such technical TCPs conducted in bulk are, for instance, the syntheses of poly(ethylene terephthalate), poly(butylene terephthalate), nylon-6, nylon-6,6 and the syntheses of polycarbonates by transesterification of bisphenols with diphenyl carbonate. In all these cases, the content of cycles is seemingly only in the order of 2-5 weight% corresponding to 5-15 mol%. However, for technical polycondensates a high molecular weight is not desired, because a high melt viscosity is unfavorable for any processing from the melt. Therefore, the conversion is usually stopped around 98-99% or chain terminators are added. Furthermore, numerous side reactions may occur at high temperatures, such as decarboxylation, formation of vinyl and ether groups, formation of five-membered cycles (e.g. tetrahydrofuran from 1,4-butanediol) and Fries-rearrangement (in the case of aromatic ester or carbonate groups). Moreover, previous studies of cycles in technical TCPs are based on extraction of cyclic oligomers. These extractions are far from complete, so that these previous studies considerably underestimate the real content of cyclic oligomers and polymers. For all these reasons the rather low content of cyclic oligomers and polymers in technical polycondensates cannot serve as serious argument against the ring-ring equilibrium theory discussed above.

Conclusion

The total equilibration of all reaction partners and products in a TCP may be described by three kinds of equilibria: chain-chain, ring-chain and ring-ring equilibria. Whereas the J.S. theory[4] and its extension by Flory[3] is focussed on ring-chain equilibria, the present study emphasizes the role of ring-ring equilibria at high conversions. Increasing conversion means higher ring/chain ratios until all linear species disappear at 100% conversion. Considering our recent theory of KCPs[22,23] the following conclusion may be drawn: "It is the fundamental tendency of all step-growth polymerizations to yield cyclic oligomers and polymers as stable endproducts. The linear chains are nothing else but the reactive intermediates". A more detailed discussion of this topic has been published.[24]

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