*Macromol. Symp.* **2003**, *199*, 1-13

# What Does Polycondensation Mean?

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**Summary:** This contribution has the function of an introduction to the entire volume. It deals with several fundamental definitions and classifications related to the chemistry of polycondensation processes, and it includes modifications of the classical theory of step-growth polymerizations.

**Keywords**: cyclic polymers, hyperbranched polymers, kinetic control, polycondensation, thermodynamic control

## Introduction

The classical theory of step-growth polymerizations as it is presented in all textbooks of polymer science is mainly based on the experimental work of Carothers[1,2] and on the theoretical contributions of Flory.[3,4] One of the milestones in polymer science which has emerged from this work is the demonstration that the reactivity of endgroups is (in general) independent of the chain length (previously denied by Staudinger and other chemists). The classical theory of polycondensation describes the chain growth of linear monomers which are symbolized as "a-b" monomers, when different endgroups are present or "a-a" and "b-b" monomers when having identical endgroups. All reactive species, including linear oligomers and polymers can react with each other at any time and the chain lengths increase with the conversion according to the "Carothers equation" (1). The influence of chain terminators (frequently added in technical syntheses to regulate the average degree of polymerization, $\overline{DP}$) or an imbalance of the stoichiometry (which has the same effect) may be expressed by eq. (2). The frequency of chains characterized by an individual DP is given by eq. (3), and corresponding mass distribution by eq. (4). In the following paragraphs further definitions and classifications will be presented along with several modifications of the classical theory of step-growth polymerization.

 DOI: 10.1002/masy.200350901

$$\overline{DP} = \frac{1}{1-p} \tag{1}$$

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

p = conversion of functional groups

$$\overline{DP} = \frac{1+r}{2r(1-p)+1-r} = 1 \tag{2}$$

with $r = N_a/N_b$ ; $N_a/N_b$ the total numbers of initially present functional groups, incl. those of the chain terminator

$$f_n = p^{n-1}(1\text{-}p) \tag{3}$$

with n = DP of individual chains

$$W_n = m_n \cdot p^{n-1}(1\text{-}p) \tag{4}$$

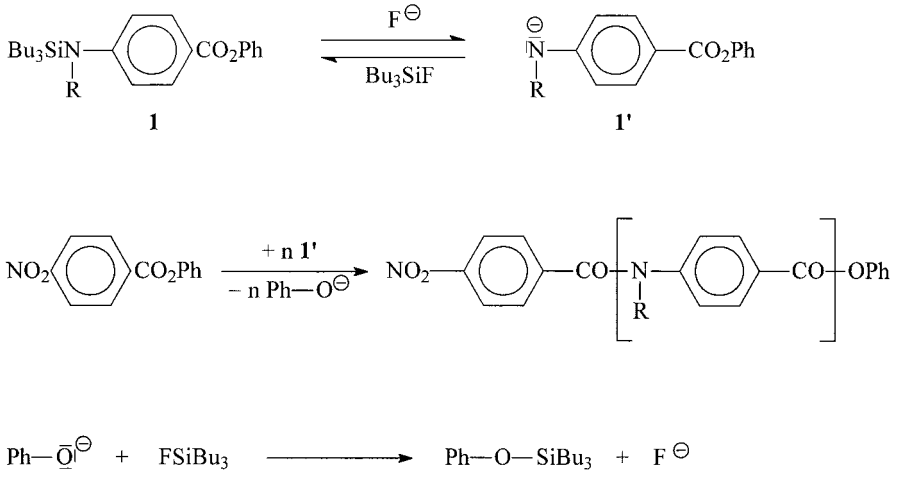
## Definitions and Classifications

### Step-growth Versus Chain-growth Polymerizations

The classical definition of polycondensation is based on two aspects: 1) elimination of a small byproduct (e.g. $H_2O$, HCl etc.) in every propagation step, 2) a step-growth kinetic resulting from an equal reactivity of all monomers, oligomers and polymers (with exceptions in the case of monomers). It is important to keep both aspects in mind, because a polymerization process obeying a chain-growth kinetic may involve elimination of small byproducts in every propagation step. In an ideal chain-growth polymerization involving elimination steps, an initiator starts the propagation, the polymers do not react with each other and the monomers exclusively react with the active chain end. However, in real experiments both kinds of kinetics may overlap, so that a clearcut classification is not always feasible. Chain-growth

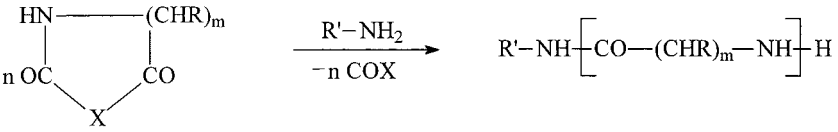
polymerizations involving condensation steps are not a curiosity, they are, in fact, the oldest polymerization process known on earth because all syntheses of biopolymers in living organism obey this reaction pattern.

Step-growth and chain-growth polymerizations involving elimination reactions in every propagation step have the same favorable thermodynamic situation, namely a reaction entropy close to zero. However, the different kinetic course has the consequence that the molecular weight distribution (MWDs) may be quite different. In a typical step-growth polymerization, the polydispersity is $\geq 2.0$, whereas in a chain-growth polymerization, narrow molecular weight distributions with polydispersities $\leq 1.1$ may be obtained. Several in vivo syntheses of biopolymers which all involve chain growth polymerizations produce in fact monodisperse biopolymers. "Polycondensations" showing a more or less pronounced tendency towards chain-growth polymerizations with condensation steps are, for instance, the oxidative coupling of ortho-disubstituted phenols[5,6] or syntheses of poly(phenylene sulfide).[7] These polymerizations involve radicals as reactive intermediates.




Scheme 1

More recent examples of chain-growth polymerizations involving condensation steps were published by Yokogawa and coworkers.[8-11] These polymerizations are based on nucleophilic substitutions of non-cyclic monomers, as exemplarily illustrated in Scheme 1. Those authors used the term "chain growth polycondensation" when the monomers exclusively reacted with an initiator and active endgroup of the growing chain. However, the long known[12] ring-opening polymerizations of cyclic amino acid anhydrides (Scheme 2) have the same kinetic and thermodynamic properties as the polymerizations of Yokosawa et al. and were defined as chain-growth (and ring-opening) polymerizations for many decades. Therefore, it is obvious that the term "polycondensation" is misleading, when applied to chain-growth polymerization, even when condensation steps are involved. The term "polycondensation" was and is defined for a polymerization process obeying a step-growth kinetic. Perhaps "chain growth condensation polymerization" is a terminology which is acceptable for polymerizations such as those outlined in Scheme 1.




X = O, S

Scheme 2

**Kinetic Control Versus Thermodynamic Control**

In all fields of chemistry the main product isolated from a reaction mixture may be the result of the most rapid reaction (kinetic control) or of an equilibration process (thermodynamic control). By coincidence the kinetically controlled reaction product may also be the thermodynamically most stable component of the reaction mixture, but in most cases it is not. In the chemistry of carbon compounds a general and systematic correlation between the kinetic and thermodynamic properties of a reaction mixture does not exist. A differentiation between a kinetically or thermodynamically controlled course can and should also be made for all polymerization processes. For instance, chain-growth polymerizations of α-olefins or

vinyl monomers are kinetically controlled polymerizations resulting in thermodynamically instable polymers, which upon equilibration would collapse into (un)substituted cyclohexanes. However, for numerous ring-opening polymerizations and polycondensations both kinetically controlled and thermodynamically controlled reaction pathways exist. For a proper understanding of structure and properties of the resulting polymers it is important to know, if they were formed under kinetic or thermodynamic control. Characteristic for a kinetically controlled polycondensation (KCP) is the point that all products formed in early stages of the polymerization are stable during the later stages. Therefore, processing of such polymers at high temperature may change structure and properties of the polymer due to the influence of equilibration reactions. Such equilibrations typically involve the formation of cyclic oligomers by "back-biting degradation".[13,14] On the other hand, any kind of ordered structure, such as alternating sequences and block copolymers can only be obtained via a KCP. Furthermore, the molecular weight distributions, MWDs, may be different. Typical for thermodynamically controlled polycondensations (TCPs) are polydispersities in the range of 2.0-2.5,[4] whereas the products of KCPs may have broader distributions. For all these reasons it is important to classify polycondensations according to kinetic or thermodynamic control.

**"a-b" Versus "a-a + b-b" Monomers**

In most textbooks "a-b" and "a-a + b-b" monomers are discussed so as if their polycondensations and the structures of their resulting polymers are quite similar. However, both monomer systems differ largely in numerous aspects and these differences should be discussed in this section. The most obvious difference (usually mentioned in textbooks) is the fact that the "a-b" monomers have a built-in perfect stoichiometry of the functional groups. Furthermore, all oligomers and polymers possess the same combination of "a" and "b" endgroups. In contrast, polycondensations of "a-a" + "b-b" monomers automatically produce mixtures of three types of endgroup combinations. This difference is important when the polymers should be subjected to chemical modifications of endgroups, chain extension or crosslinking reactions.

Particularly important is the point that "a-b" monomers possess a considerably greater potential for syntheses of functional polymers and complex architectures.[15] For instance,

addition of "a-a" or "b-b" monomers to a larger quantity of "a-b" monomers yields oligomers or polymers having either two "a" or two "b" endgroups.[16,17] Furthermore, the feed ratio of "a-b"/"a-a" (or "a-b"/"b-b") monomers allows a control of the $\overline{DP}$. The resulting telechelic polymers may be used as central blocks in syntheses of A-B-A triblock copolymers[18] or as components of multiblock copolymers. Secondly, copolycondensations of "$a_n$" monomers with an excess of "a-b" monomers yields star-shaped polymers. The number of the star arms depends on the functionality of "$a_n$" and the lengths of the star arms on the "a-b"/"$a_n$" ratio. In contrast the combination of "$a_n$" with "a-a" and "b-b" monomers yields networks. Thirdly, cocondensations of "a-$b_n$" + "a-b" monomers yield hyperbranched copolymers with variation of the branching density.[3,4,19,20,21] The presence of "b-b" monomers results again in crosslinking. Last but not least, all species in a sample of "a-b" type oligomers and polymers can, in principle, cyclize (see below), whereas in the "a-a" + "b-b" case 50% of the reaction products cannot cyclize. In summary, a classification of polycondensations based on "a-b" monomers and others based on "a-a" + "b-b" monomers is reasonable because of the quite different synthetic potential.

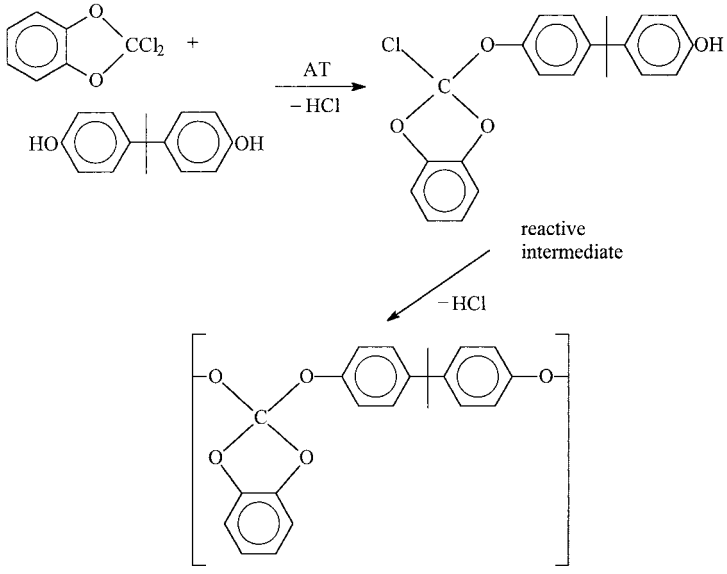
**Stoichiometric Versus Non-stoichiometric Polycondensations**

According to the classical theory of step-growth polymerizations, the highest molecular weights are obtained with a perfect 1:1 stoichiometry of the functional groups . However, in real polycondensations of "a-a" + "b-b" monomers it was found that an excess of one monomer may give higher molecular weights than the 1:1 feed ratio. For a proper understanding of so-called non-stoichiometric polycondensation, the first question which needs clarification is the structure (or composition) of the polymer. If the molar ratio of A and B units in the polymer backbone is 1:1, the chain growth was necessarily a stoichiometric process, even when the feed ratio was far from 1:1. Three reasons may account for the observation that an excess of one monomer in the feed may give optimum molecular weights of a perfectly stoichiometric polymer:

1) Side reactions of one monomer which do not significantly disturb the chain growth. A typical example is the hydrolysis of phosgene in the interfacial syntheses of polycarbonates, which is compensated by an excess of phosgene.

2) Physical reasons hindering one monomer to participate completely in the chain growth process. Such physical reasons are: distillation or sublimation from the reaction mixture, adsorption on a solid surface or complexation with solvents or other components of the reaction mixture.

3) A two-step propagation kinetic with a faster second step. This means that an intermediate is formed with a functional group which is more reactive than either the "a-a" or the "b-b" monomer. Therefore, an excess of the less reactive monomer will accelerate the chain growth and the degree of polymerization will be considerably higher than expected from the imbalance of the stoichiometry according to the classical theory. However, a 1:1 feed ratio will give the highest molecular weight, when the reaction time allows for high conversion . The polycondensation of 2,2-dichloro-4,5-benzodioxolane with diphenols (Scheme 3) is a typical example of such a non-stoichiometric polycondensation.[22] Another example is presented by M. Ueda and coworkers in this book below.




Scheme 3

**Cyclic Monomers and Ring-opening Polycondensations**

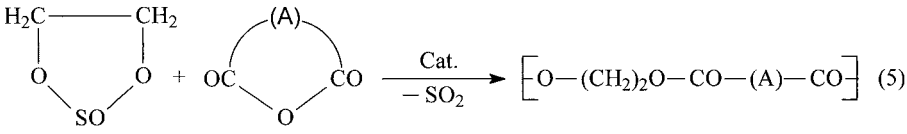
The experimental work of Carothers and Flory and the classical theory of polycondensation is based on linear or branched monomers. However, any kind of heterocycles containing at least two reactive bonds may, in principle, be used as monomers for "ring-opening polycondensation". None the less, in textbooks of polymer science cyclic monomers are exclusively discussed in connection with ring-opening polymerizations involving chain growth kinetics. Cyclic monomers can be used for polycondensations in two different combinations:

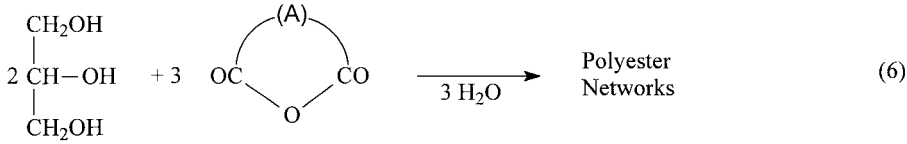
(I) Cyclic monomer + linear monomer

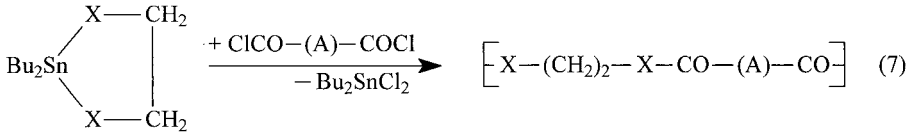
(II) Cyclic "a-a" monomer + cyclic "b-b" monomer.

The former combination (I) is far more versatile and allows for a much broader application of cyclic monomers than case (II) for which only one successful combination (eq. (5)) has recently been reported[23].

A versatile and commercial class of cyclic monomers useful for polycondensation are cyclic anhydrides. Polyester resins based on polycondensations of cyclic anhydrides and glycerol (or other polyols) were studied and commercialized more than seven decades ago (eq. (6)),[24] and quite recently resins based on hyperbranched poly(ester amide)s were developed.[25] Another group of versatile cyclic monomers containing Sn atoms has recently been explored by the author.[26,27] The Sn atom enhances the nucleophilicity of neighboring heteroatoms, and thus, favors polycondensations with various electrophilic "b-b" type monomers as exemplified in eq. (7). Numerous Sn containing heterocycles are easy to synthesize and they have the important advantage to allow for a combination of ring-opening polymerization and polycondensation in "one-pot procedures".[26] All ring-opening polycondensations have in common that their thermodynamic properties deviate from those of polycondensations exclusively involving linear monomers. In most cases (typical for combination (I)) the reaction entropy is negative.[26] In case (II) the reaction entropy depends very much on the ring size and $\Delta S$ may turn positive, but such a case has not been realized yet.[23]




X = O, S

**Cyclic Versus Linear Polymers**

For reasons discussed by Carothers[1] and Flory[3] those authors did not consider cyclization reactions to play an important role in their theory of step-growth polymerizations. In 1950 Jacobson and Stockmayer[13,14] proved that at least cyclic oligomers are formed in all TCPs due to "back-biting degradation" and they developed a mathematical treatment of equilibrium concentrations and molecular weight distribution of the cycles. More recently, theoretical calculations of KCPs (presented by Stepto[28,29] and Gordon et al.[30]) and experimental results obtained by MALDI-TOF mass spectroscopy (reported by Kricheldorf et al.[31-34]) proved that ring closure reactions play a decisive role in KCPs. Cyclization competes with propagation at any concentration and at any stage of a polycondensation. In an ideal KCP (free of side reactions and perfect stoichiometry) all reaction products will be cycles at 100% conversion.

Therefore eq. (1) needs to be replaced by eq. (8) and eq. (3) should be replaced by eq. (9), and the following consequences have to be considered.

$$\overline{DP} = \frac{1}{1 - p\left(1 - \frac{1}{X^{\alpha}}\right)} \tag{8}$$

with $\alpha = V_p/V_c$ ratio of propagation and cyclization rate

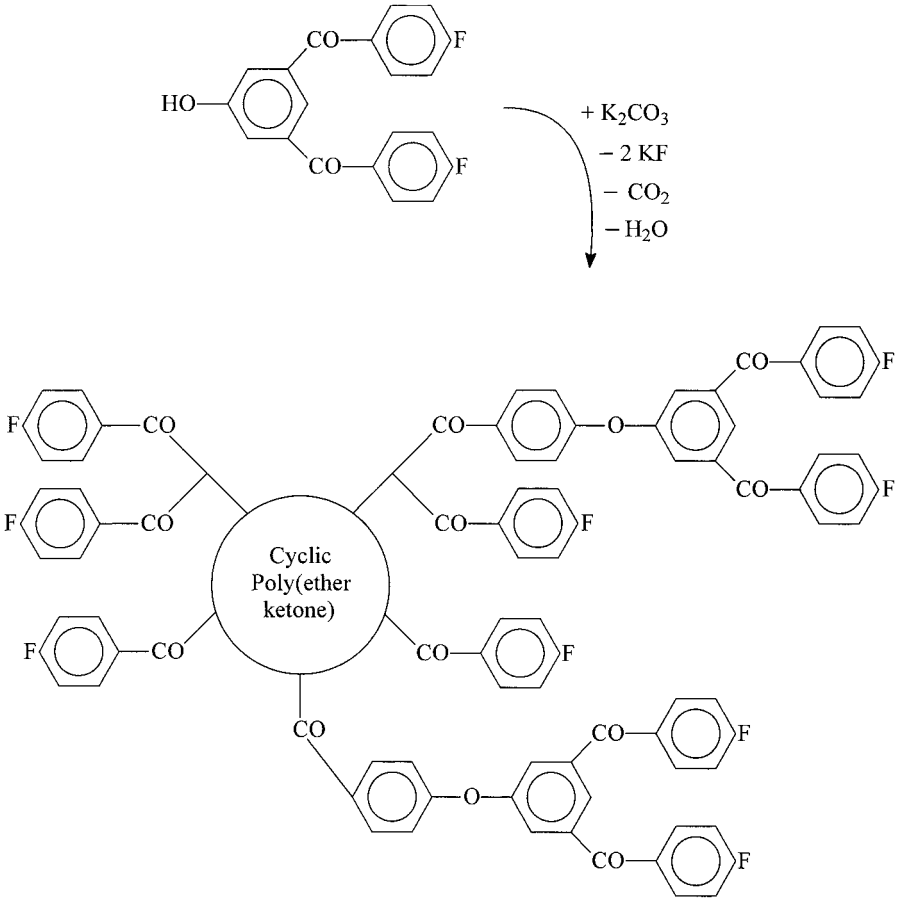
$X$ = constant $> 1.0$ allowing for adaptation of the equation to individual experiments with variation of the concentration

$$\overline{DP} = \frac{1 + r}{2r\left[1 - p\left(1 - \frac{1}{X^{\alpha}}\right)\right] + 1 - r} - 1 \tag{9}$$

Firstly, in real experiments involving a few side reactions and conversions below 100%, neither 100% cycles nor 100% linear chains will be obtained. Secondly, the rate of cyclization is decisive for the maximum molecular weight which can be obtained. The infinite molecular weight predicted by the classical "Carothers equation" (1) can never be achieved, even under ideal conditions. Thirdly, the MWDs are different from those of the classical theory formulated by Flory in eqs. (3) and (4). Fourthly, the "cascade theory"[3,4] describing the formation of hyperbranched polymers by polycondensation of "a-$b_n$" monomers also needs modification, because it does not include a consideration of cyclization reactions.

The polycondensation of an "a-$b_n$" monomer creates oligomers and polymers possessing one "a" and numerous "b" functional groups. Therefore, cyclization can compete with propagation at any stage of the polycondensation and eq. (8) is also valid for "a-$b_n$" monomers. Both chain growth and polydispersity are limited by the influence of cyclization in contrast to the calculations of Flory.[3,4] At 100% conversion all reaction products are cycles with hyperbranched side chains (Scheme 4).[35] The tree-shaped structures depicted in previous

publications of numerous authors just present an intermediate state of an incomplete or imperfect polycondensation. The permanent competition of cyclization and propagation has also a strong influence on the structure of branched or crosslinked polymers resulting from KCPs of "$a_n$" + "b-b" monomers. However, because of the limited space of this article the rather complex course of "$a_n$" + "b-b" polycondensations should not be discussed here in more detail.




Scheme 4

## Conclusion

The historical merits and the importance of the classical theory of step-growth polymerizations as elaborated by Carothers and Flory can never be overestimated. None the less, numerous experimental results and theoretical considerations which emerged over the past fifty years require revision, modification and expansion of the classical theory.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