



# What Does Conversion Mean in Polymer Science?

Hans R. Kricheldorf,\* Felix Scheliga, and Steffen M. Weidner

The definition of the term “conversion” is discussed for a variety of polymer syntheses. It is demonstrated that in contrast to organic and inorganic chemistry several different definitions are needed in polymer science. The influence of increasing conversion on structure and topology of homo- and copolymers is illustrated. Chain-growth polymerizations, such as radical polymerization or living anionic polymerizations of vinyl monomers, condensative chain polymerization, two and three-dimensional step-growth polymerizations, ring–ring or chain–chain equilibration and chemical modification of polymers are considered.

## 1. Introduction

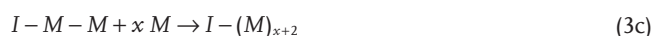
In more than 99% of all reactions in organic and inorganic chemistry the term “conversion” ( $p$ ) deserves only one simple definition, which is presented in Equation (2), based on the reaction scheme given in Equation (1). Conversion means consumption of a starting material needed for the reaction under consideration. Quantitative conversion represents an experimental situation defined by the total consumption of a starting material ( $A$  or  $B = 0$  in Equation (2)). However, under perfectly homogeneous conditions, or in other words, in a one-phase system, all chemical reactions are part of an equilibrium, and quantitative conversion cannot be reached. Only in experiments where at least one reaction product can migrate to another phase (e.g., by evaporation or crystallization), quantitative conversion can be achieved. However, for preparative studies an extremely one-sided equilibrium may be treated as a quantitative reaction. It is also trivial to say that a quantitative consumption of a starting material may result from side reactions, but

definitions of conversions as they are discussed here and in text books make only sense with regard to the desired main reaction, which is usually formulated in the text:

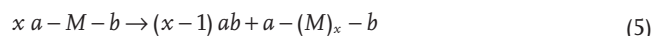


$$p = (N_{A0} - N_{At}) / N_{A0} \quad (2)$$

(with  $N_A$  = number of A molecules)



$$p = (N_{M0} - N_{Mt}) / N_{M0} \quad (\text{with } N_M = \text{number of monomers}) \quad (4)$$



$$p = (N_{a0} - N_{at}) / N_{a0} \quad (6a)$$

(with  $N_a$  = number of functional “a” groups)

$$p = (N_{b0} - N_{bt}) / N_{b0} \quad (6b)$$

(with  $N_b$  = number of functional “b” groups)

Since Carothers<sup>[1]</sup> and Flory<sup>[2,3]</sup> have subdivided all polymerizations into two categories—chain-growth and step-growth polymerizations—textbooks of polymer science usually mention two different definitions of “conversion.” The definition of Equation (4) is presented for chain-growth polymerizations (ChainGP), a schematic formulation of which is given in Equations (3a–c). Concrete examples are the anionic polymerizations of oxirane, cyclo(hexamethyl trisiloxane), and methyl methacrylate in **Scheme 1** For linear step-growth polymerizations (StepGP), a schematic formulation of which is given in Equation (5) and concrete examples in **Scheme 2** the conversion is defined by Equation (6a,b). Equation (6a,b) are identical, when “a-b” monomers (Equation (5)) or equal amounts of  $a_2$  and  $b_2$  monomers are used. For  $b_2 > a_2$  only Equation (6a) holds. However, polymer science and the chemistry of small molecules not only differ in the sheer number of definitions needed for the term “conversion.” In organic and inorganic chemistry the extent of conversion mainly influences the yield and indirectly the purity of the desired reaction product. But, in polymer science the conversion also has a strong influence on several structural parameters, such as:

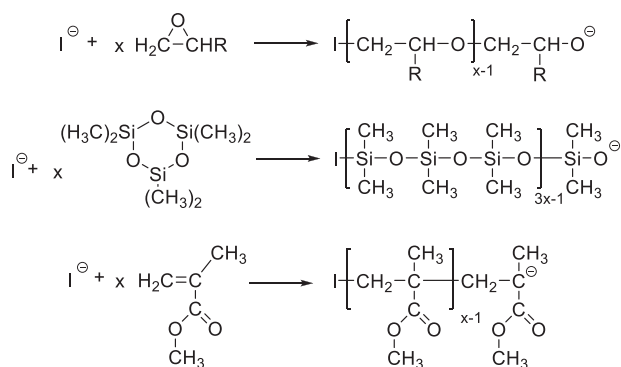
Prof. H. R. Kricheldorf, Dr. F. Scheliga  
 Universität Hamburg  
 Institut für Technische und Makromolekulare Chemie  
 Bundesstr. 45, Hamburg D 20146, Germany  
 E-mail: hrkricheldorf@aol.de

Dr. S. M. Weidner  
 BAM – Bundesanstalt für Materialforschung und -prüfung  
 6.3 Strukturanalytik  
 Richard Willstätter Str. 11, Berlin D-12489, Germany

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/macp.202100010>.

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**Scheme 1.** Examples of anionic polymerizations involving oxiranes, hexamethyl cyclotrisiloxane or methyl methacrylate as monomers (I = anionic initiator).

- the number average molecular weight ( $M_n$ ), and the weight average molecular weight ( $M_w$ ) and thus, on their ratio (dispersity  $\mathcal{D}$ ), which is a simple indicator for a broad or narrow molecular weight distribution,
- the structure of hyperbranched polymers, because the degree of branching increases with the conversion,
- the structure of copolymers, because both ratio and sequence of comonomers vary with the conversion when the reactivity of the comonomers is (as usual) not identical,
- the architecture (topology), because in StepGP cyclization occurs, the extent of which increases with the conversion,
- the architecture (topology) of branched polymers resulting from “three-dimensional” polycondensations, because beyond a critical conversion insoluble networks (gels) are formed.

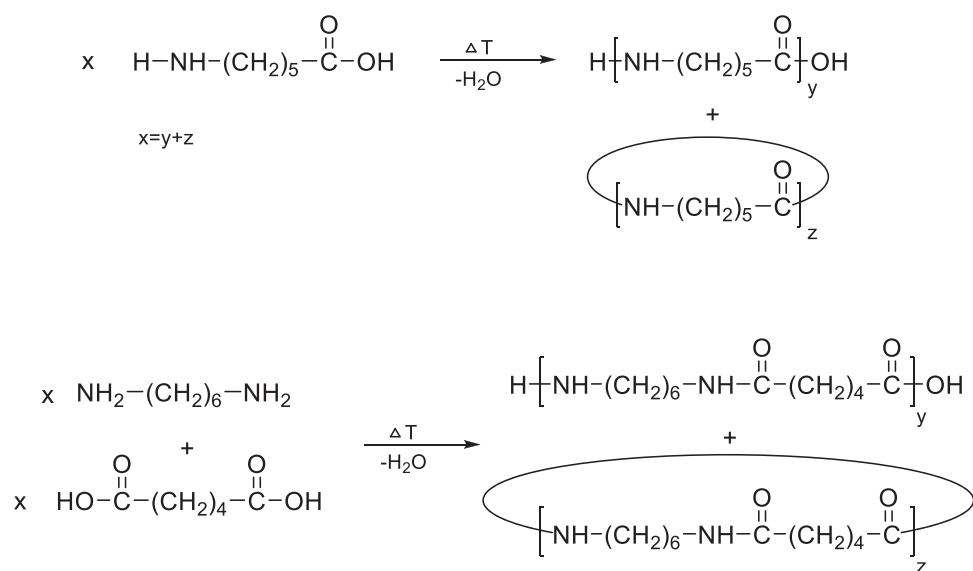
This list clearly demonstrates that in polymer science the role of conversion is far more complex than in almost all reactions of small molecules. A systematic discussion of conversion

and structure of the resulting (co)polymers is rarely found in textbooks and over the past 20 years new polymerization strategies (e.g. ring-expansion polymerization and ring-ring or polymer equilibration) have been developed, which require additional definitions of conversion. The present contribution has the purpose to close this gap.

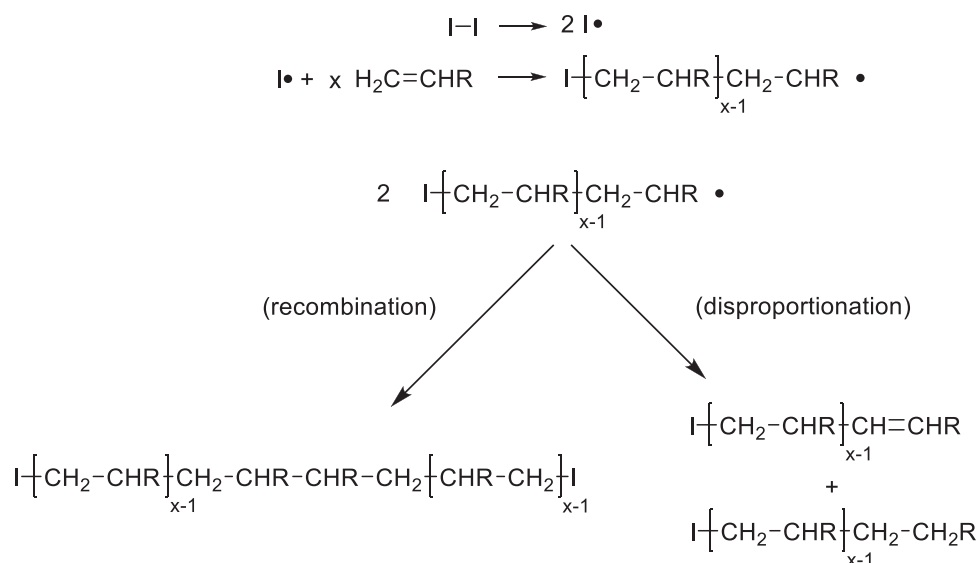
## 2. Chain-Growth Polymerizations

The definition of conversion used for ChainGP (Equation (4)) is quite analogous to the definition used for reactions in organic and inorganic chemistry (Equation (2)). Likewise, analogous are the consequences of homogeneous and heterogeneous reaction conditions. In a one-phasic system the conversion stops, when the equilibrium concentration of monomer has been reached, and a nearly quantitative conversion may be achieved, when the polymer precipitates from the reaction mixture or when it crystallizes from a polymerization performed in the melt. Side reactions destroying the active chain ends will, of course, prevent high conversions regardless if the reaction mixture remains homogeneous or not.

Yet, there is one important type of polymerization which deviates from the afore mentioned scheme, namely radical polymerizations of vinyl monomers. As schematically outlined in **Scheme 3**, the chain growth is followed by two kinds of unavoidable termination steps: recombination and disproportionation. Disproportionation cannot occur, when the  $\beta$ -carbon of the vinyl monomer is double substituted, as it is true for esters of methacrylic acid (**Scheme 4**). When enough initiator is present, which produces radicals for a sufficiently long period of time, quantitative conversion of the vinyl monomers may be achieved. Furthermore, high molecular weights may be obtained, because the propagation is usually much faster than the termination steps. The average molecular weights are strongly influenced by the temperature, as discussed in all



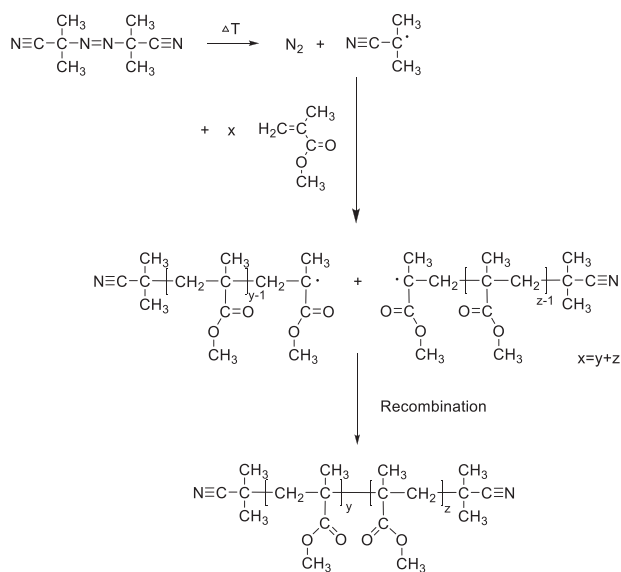
**Scheme 2.** Syntheses of Nylon-6 and Nylon-6,6 by thermal polycondensation.



**Scheme 3.** Fundamental reactions of a free radical polymerization of vinyl monomers.

textbooks, whereas the conversion has little influence on the lengths of the polymer chains.

In the case of radical copolymerizations of two comonomers having different reactivities (as usual), the conversion may have a strong influence on the composition of the resulting copolymers. The chains formed in an early stage of the copolymerization contain a larger fraction of the more reactive monomer and the chains formed at high conversions necessarily consist of a larger fraction of the less reactive comonomer. This phenomenon is known under the term “first order heterogeneity.” It is obvious that the composition of the entire polymerization product, and hence, its physical and mechanical properties will be affected, when the conversion is incomplete.



**Scheme 4.** Radical polymerization of methyl methacrylate initiated by the radicals liberated from azoisobutyronitrile.

When in anionic polymerizations termination steps are absent, the chain growth will continue until the monomer/polymer equilibrium is reached and the  $DP$  will parallel the monomer/initiator ratio as formulated in Equation (7). In this case the maximum  $DP$  will be reached at 100% conversion. Two groups of such ideal polymerization are known based on the following criteria. First, initiation is much faster than propagation and all chains are initiated almost at the same time. In this case a narrow molecular weight distribution will result ( $M_w/M_n < 1.2$ ). This group of polymerizations, first detected by Michael Swarc<sup>[4]</sup> for anionic polymerizations of certain vinyl monomers, has been labeled “living polymerization.” Three of such almost ideal polymerizations are outlined in Scheme 1 Second, not all chains are initiated at the same time, so that a broad molecular weight distribution will result. This case is nick-named “immortal polymerization”

$$DP = ([M]/[I]) \cdot p \quad (7)$$

In the case of an (nearly) ideal ionic copolymerization of monomer having different reactivities with initiation faster than propagation, the chain segment following the end groups formed by the initiator, will contain a larger fraction of the more reactive monomer. With increasing conversion incorporation of the less reactive monomer becomes more and more effective and the segments formed toward the end of the polymerization will be richer in units of the less reactive monomer. This phenomenon is called “second-order heterogeneity.” In such copolymerizations the “first-order heterogeneity” will not be totally absent, but its influence on the properties of the copolymer will be small compared to the influence of the “second-order heterogeneity.” Incomplete conversion will again affect the physical and mechanical properties of the copolymers, because the balance between the two comonomers is different from that of a copolymer resulting from 100% conversion.

### 3. Step-Growth Polymerizations

#### 3.1. Two-Dimensional Step-Growth Polymerizations

The experimental and theoretical basis of StepGP was elaborated by W. H. Carothers and coworkers in 1927–1937,<sup>[1]</sup> and later expanded and improved by J. P. Flory (Nobel Prize 1974).<sup>[2,3]</sup> Further important revisions and improvements were contributed by Jacobson and Stockmayer,<sup>[5,6]</sup> Gordon and Temple<sup>[7,8]</sup> and Stepto and coworkers.<sup>[9,10]</sup> The description of StepGP in textbooks is mainly based on the Carothers-Flory (CF) theory, whereas the later contributions of other researchers are usually ignored. Characteristic of the CF theory are the assumptions that:

- all monomers, oligomers and polymers can react with each other at any time (kinetic definition of StepGP),
- cyclization reactions do not play any role (which was revised later by Stockmayer, Gordon and Stepto).

Prior to a discussion of the CF-theory, three terms should be defined to avoid confusion. First, following Flory's terminology, StepGPs involving monomers having two functional groups will be called "two-dimensional," whereas StepGPs based on monomers having three or more functional groups will be called "three-dimensional," because they may yield space-filling networks. Second, StepGPs exclusively yielding linear chains (according to the CF-theory) will be labeled "linear polycondensations" (or linear polyadditions). Third, kinetically controlled (kin-c) and thermodynamically controlled (therm-c) StepGPs should be distinguished.

Kin-c means that the main reaction product is formed by the most rapid reaction sequence, and that the individual polymerization steps are irreversible. Cyclics formed in the course of a kin-c polymerization are not reactive and just play the role of solvents.

Therm-c means that the polymerization process involves rapid equilibration reactions, so that in the ideal case a reaction mixture represents at any time the thermodynamically most stable scenario. These therm-c polycondensations or polyadditions involve formation of cyclic oligomers via "back-biting" from a reactive chain end. This ring-forming process is reversible, and the resulting ring-chain equilibrium automatically includes a ring-ring and a chain-chain equilibrium.

The differentiation between kin-c and therm-c type StepGPs was contributed to the theory of StepGPs by Jacobson and Stockmayer.<sup>[5,6]</sup>

The final state of a perfectly linear kin-c polycondensation is one giant chain comprising all monomers. Since this chain contains two end groups (as any linear chain), it does not obey the definition of quantitative conversion ( $p = 1$ ) according to Equation (6a,b). It is an irony of the CF theory that its definition of conversion is useful for StepGPs involving cyclization, because 100% conversion can only be achieved with complete cyclization of all reaction products. However, this is in contradiction to the postulated perfectly linear character. In principle a maximum conversion of a perfectly linear polycondensation may be defined according to Equation (6a) with the restriction that  $N_{a_i} \geq 1$  (Equation (8a)) or according to Equation (8b). This modification takes into account that the presence of two end groups represents the final state. Nonetheless, Equation (6a,b)

is a useful approximation for both, kin-c and therm-c polycondensations up to conversions near 99%. It is perfectly correct for StepGPs involving cyclization, as demonstrated by the consideration of 100% conversion. Since at 100% conversion, no end groups have survived, the reaction mixture will exclusively consist of cycles. These cycles are, of course, not formed at once at the end of the polycondensation, they are formed gradually over the whole course of the polycondensation. Thus, the weight fraction of cycles increases dramatically between 99% and 100% conversion, because in this range the long chains cyclize. Therefore, it is characteristic for StepGPs that the architecture of the reaction products changes gradually from linear to cyclic until at 100% conversion all reaction products are cycles:<sup>[11]</sup>

$$p_{max} = (N_{a0} - N_{a_i})/N_{a0} \quad \text{with } N_{a_i} > 1 \quad (8a)$$

$$p_{max} = (N_{f0} - N_{f_\beta})/N_{f0} \quad \text{with } N_{f_\beta} > 2 \quad (8b)$$

( $N_f$  = Number of all functional groups)

The so-called "Carother equation" (9) correlates the  $DP$  with the conversion based on the definition of " $p$ " according to Equation (6a,b). Since its "invention" by W. H. Carothers it is presented in most textbooks having a chapter on StepGPs. Yet, even in the case of a perfectly linear polycondensation (as assumed by Carothers and Flory) it is not quite correct, because for  $p = 1$  it predicts a polymer chain of infinite length. However, it yields an adequate description of linear kin-c type StepGPs, when Equation (8a,b) is used. In this case the  $DP$  corresponds at  $p_{max}$  to a chain comprising all monomer units. However, as soon as formation of cycles comes into play, the "Carother equation" is pretty inaccurate. This conclusion is immediately evident in the case of therm-c type StepGPs, because in this case cyclic oligomers are formed via "back-biting" even at low conversions:

$$DP = 1/(1 - p) \quad (9)$$

$$DP = 1/[1 - p(1 - X^{-\alpha})] \quad (10)$$

with  $\alpha = \nu_c/\nu_r$  ( $\nu_r$  = rate of ring formation;  $\nu_c$  = rate of chain growth)

Kinetic calculations of Gordon and Stepto<sup>[7-10]</sup> and the experimental work of the first author<sup>[11-15]</sup> have proven, that in real kin-c StepGPs cyclization competes with chain-growth at any stage of the polymerization. At 100% conversion all end groups have disappeared, so that all reaction products have a cyclic topology. Equation (10) is then an adequate correlation of  $DP$  and conversion, because it takes into account the permanent competition of cyclization and chain growth ( $\nu_r/\nu_c$ ). For  $\nu_r = 0$ , Equation (10) is identical with Equation (9). For  $\nu_r > 0$  and under ideal conditions the  $DP$  is exclusively limited by the impact of cyclization. However,  $\nu_c/\nu_r$  is not absolutely constant over the whole course of the polycondensation. It varies slightly with the conversion, because the molar concentration of all linear species  $[La]$  decreases dramatically at higher conversion (Equation 11). This equation is the so-called "law of

self-dilution<sup>[16]</sup> which is characteristic for StepGPs in contrast to ChainGPs.  $[L_a]$  decreases with higher conversions regardless if the conversion results from cyclization or from chain growth steps. The lower concentration favors, in turn, cyclization according to the Ruggli–Ziegler Dilution Principle. On the other hand, the increasing chain length reduces the cyclization tendency. The balance between both effects depends on the chemical structure of the resulting polymer and on the solvation, which influences the coil density of a polymer chain and thus, the distance between the end groups:

$$[L_a]_t = [L_a]_0 (1 - p)$$

( $[L_a]$  = molar concentration of all linear active species)

(11)

Jacobson and Stockmayer<sup>[5,6]</sup> have denied that end-to-end cyclization occurs in reversible (therm-c) polycondensations with exception of very low oligomers. They have calculated that for most monomers polycondensations with high monomer concentrations (e.g., in bulk) will only result in low concentrations of cycles. However, it has quite recently been demonstrated<sup>[17,18]</sup> that part of the Jacobson–Stockmayer theory is wrong, and end-to-end cyclization can occur under all reaction conditions, so that 100% conversion with formation of 100% cycles can also theoretically be achieved in therm-c polycondensations. Hence, the definitions (6a) and (6b) serve, in fact, all types of StepGPs.

In contrast to ionic polymerizations of  $\alpha$ -olefins, vinyl monomers or heterocycles increasing conversion influences two structural parameters of polycondensates, namely the molecular weight and the topology. However, for the following reasons the influence of increasing fractions of cyclic polymers on the properties of polycondensates is usual not observed in technical products. The weight fraction of cyclic polymers, above all high molar mass cycles, increases strongly above 99.9% conversion. Yet, extreme conversions also mean extreme molar masses of the entire polycondensate. Since almost all polycondensates are polar polymers, the melt viscosity may reach levels, which make processing from the melt difficult or even impossible. Hence, the number average molecular weights of polycondensates are usually kept below 50 000 and even below 20 000, for example by the addition of chain terminators. Regardless how the conversion was stopped, any limitation of the conversion has the consequence, that the fraction of cycles is kept on a low level (typically <5 weight%).

StepGPs need a further differentiation, namely systems based on “*a-b*” monomers (see Nylon-6 in Scheme 2 and systems based on “ $a_2 + b_2$ ” combinations (see Nylon-6,6 in Scheme 2. Usually, the only comment in textbooks is the statement that “*a-b*” monomers have the advantage of a built-in perfect stoichiometry of “*a*” and “*b*” functional groups. However, in a recent Feature Article<sup>[19]</sup> the first author has pointed out that both systems vary largely in their synthetic potential, meaning that with a combination of “ $a_2$ ” and “ $b_2$ ” monomers a much broader variety of structures and architectures can be synthesized. Yet, both monomer systems may also vary with respect to the kinetic course, Thus, the cyclization tendency of “*a-b*” monomers is twice as high, when length and structure of these monomers are comparable with those of the “ $a_2$ ” and

“ $b_2$ ” monomers. This difference results from the fact that all reaction products of “*a-b*” monomers possess one “*a*” and one “*b*” end group and can cyclize, whereas in the case of an “ $a_2 + b_2$ ” polycondensation only 50% of all oligomers and polymers possess one “*a*” and one “*b*” end group. Therefore, the “ $a_2 + b_2$ ” system may be subdivided into three categories according to their kinetic properties.

- I) The reaction between both monomers is nearly as fast as the chain growth steps.
- II) The reaction between the monomers is faster than the chain growth steps.
- III) The reaction between both monomers is slower than the chain growth steps.

Category I agrees with polycondensations of “*a-b*” monomers provided that a perfect 1.0/1.0 stoichiometry of “ $a_2$ ” and “ $b_2$ ” is given, and the same definitions of conversion can be applied (Equations (6a,b and 8)).

Category II means that the monomers generate rapidly a high concentration of dimers which then continue chain growth in the normal way. Again Equations (6a,b and 8a,b) are applicable. In an extreme but unrealistic case, when the reaction between both monomers is several hundreds or even thousand times faster than chain growth, a stage will be reached where the conversion of monomers comes close to 100%, whereas the conversion of functional groups is only around 50%. This scenario underlines the difference between the definitions of Equations (4 and 6a,b).

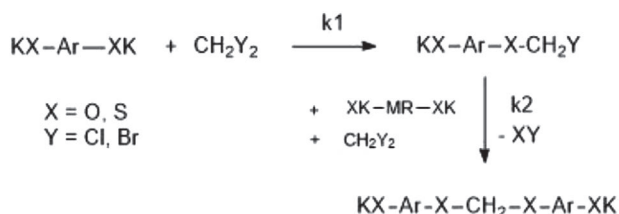
Category III means that the reaction between “ $a_2$ ” and “ $b_2$ ” monomers is the step that determines the rate of the entire polymerization process. When we assume that “ $b_2$ ” is less reactive than the “*b*” end groups of the oligomers and polymers, as illustrated for the C-Cl or C-Br bond in **Scheme 5** with  $k_1 < k_2$ ,<sup>[20–22]</sup> an excess of “ $b_2$ ” monomers enhances both, the rate of chain growth and the *DP*. Such polymerizations are known under the label “non-stoichiometric polycondensations,” but only a few examples have been described so far.<sup>[23]</sup> When an excess of “ $b_2$ ” is used, only Equation (6a) is a correct definition of the conversion, but not (6b).

Finally, Equation (12) needs a short discussion. This equation was elaborated by Flory to describe the number distribution of linear chains in kin-c StepGPs. The conversion was defined according to Equation (6a,b). For quantitative conversion Equation (12) yields  $n_x = 0$ , what means that all linear species have completely disappeared. This result may either considered as an absurdity or as an indication that finally all chains have cyclized – in contrast to Flory's postulate. However, when cyclization competes with chain growth, Equation (12) is not valid anymore for the entire molecular weight distribution, but only for the fraction of the linear chains. Nonetheless, Equation (12) may serve as an approximation to systems with low cyclization tendency (low  $v_c/v_c$  ratios, e.g. 1/100) and for conversions below 99%. Yet, Equation (12) is still correct for perfectly linear StepGPs of the kin-c type, when the conversion is defined according to Equation (8a,b).

$$n_x = p^{x-1} (1 - p)$$

(with  $x$  = degree of polymerization of individual chains)

(12)

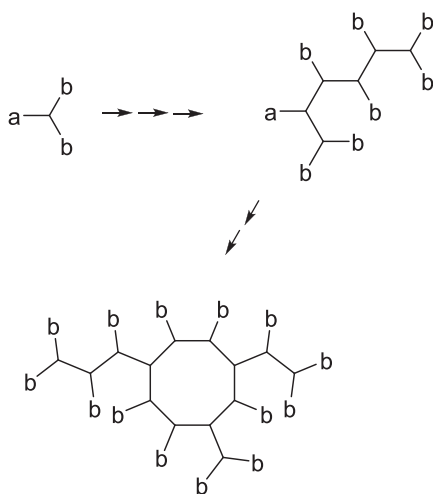


**Scheme 5.** Syntheses of poly(thio)formals from potassium salts of diphenols or bis-thiophenols and di-chloro-or di-bromo-methane.

### 3.2. Three-Dimensional Polycondensations

Three-dimensional polycondensations may be subdivided into two groups, namely those based on “ $ab_n$ ” monomers and those based on “ $a_2 + b_n$ ” monomers (with  $n > 2$ ). Monomers of the “ $ab_n$ ” types yield hyperbranched polymers that are characterized by a brush or tree-like branching (see **Scheme 6**). Hence, the conversion is best defined by the consumption of “ $a$ ” groups according to Equation (6a). Flory discussed polycondensations of “ $ab_n$ ” monomers bare of cyclization reactions,<sup>[2,3]</sup> but for such polycondensations quantitative conversion is impossible quite analogous to a perfect linear polycondensation. Hence, the restriction  $N_a > 2$  needs to be added and only a  $p_{\max}$  can be defined (Equation (8a)), but not a quantitative conversion. A quantitative conversion can only result from cyclization reactions, and recent experiments have confirmed that in polycondensations of “ $ab_n$ ” monomers cyclization competes with chain growth in close analogy to two-dimensional polycondensations. This means, that for  $p = 1$  all hyperbranched polymers possess a cyclic core (Scheme 6), and not the brush or tree-shaped architecture postulated by Flory (see also the TOC graphic). Again, in analogy to two-dimensional polycondensation, the  $DP$  obeys Equation (10) and not Equation (9).

For polycondensations of “ $a_2 + b_n$ ” monomers only the kin-c type of equifunctional monomer mixtures should be considered. Equifunctional means that the molar ratio of “ $a_2$ ” and “ $b_n$ ” corresponds to equal numbers of reactive “ $a$ ” and “ $b$ ” groups.



**Scheme 6.** Formation of hyperbranched oligomers and polymers by polycondensation of “ $ab_2$ ” monomers.

When the conversion is defined according to Equation (6a,b), the experimental conditions yield two different scenarios. First, above a critical monomer concentration gelation occurs at higher conversions and quantitative conversion cannot be achieved. For kin-c type polycondensations based on equifunctional monomer mixtures Flory has calculated the critical conversion ( $p_{cr}$ ) where the gel point is reached (Equations (13 and 14)) assuming that no cyclization occurs. This critical concentration decreases with the number of functional groups in the “ $b_n$ ” monomer. In other words, higher functionality of “ $b_n$ ” means higher crosslinking tendency. The experimental results known at that time gave slightly higher  $p_{cr}$  values than calculated by Flory. He attributed this discrepancy to a few cyclization reactions. Yet, it is also worth noting that the conversion not totally stops at the gel point. Only a part of the polycondensate is engaged in the gelation process, and the soluble oligomers and polymers can slowly continue chain growth. The real conversion will extend beyond that calculated for the gel point and will increase with time and temperature. Therefore, a general formula allowing for the calculation of the maximum conversion cannot be given:

$$\alpha_{cr} = 1/n - 1 \quad (13)$$

(with  $n$  = number of functional groups in  $b_n$ )

$$\alpha_{cr} = rp_a^2 = pb_2/r \quad (14)$$

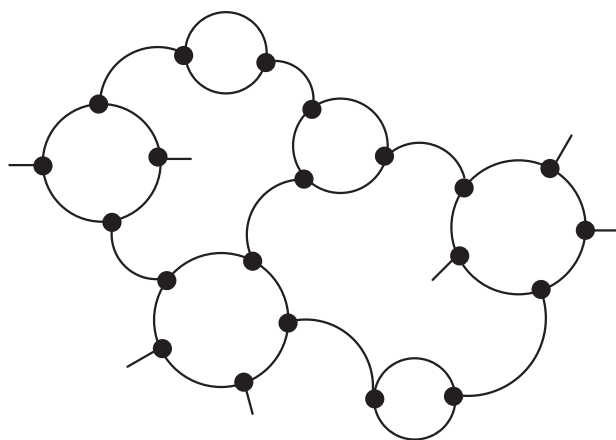
(with  $r = a/b$ ;  $p_a$  and  $p_b$  = conversion of “ $a$ ” or “ $b$ ” groups)

The second scenario concerns kin-c polycondensations performed below the critical initial monomer concentration, with the consequence that all reaction products stay in solution regardless of the conversion. For this scenario the definition of Equation (6a,b) is still useful, and in principle, quantitative conversions can be reached. In this case  $p = 1$  means that all reaction products are perfect multicyclic oligomers and polymers. **Scheme 7** presents a two-dimensional schematic illustration of a multicyclic polymer resulting from an “ $a_2 + b_3$ ” polycondensation (the three-dimensional architecture resembles that of a sponge). Experiments coming close to this ideal case were published by the first author.<sup>[24,25]</sup>

### 3.3. Combinations of ChainGPs and StepGPs

#### 3.3.1. Condensative Chain Polymerization

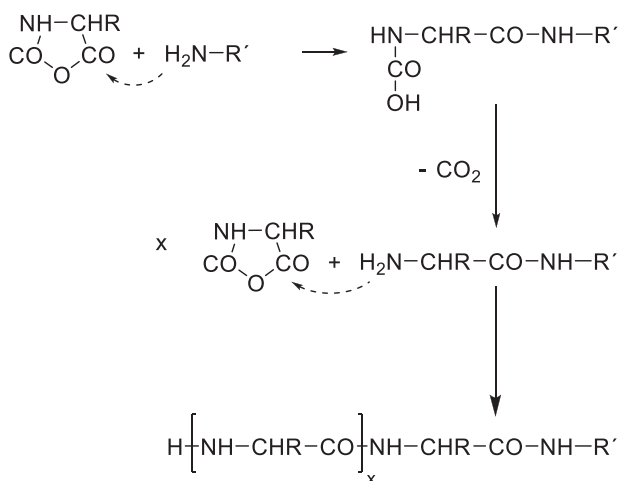
Two categories of polymerizations were detected which simultaneously involve elements of ChainGP and StepGP reactions. One group called “condensative chain (CC) polymerization” according to IUPAC rules is known for a long time and should be discussed first. Like almost all ChainGPs all growing steps of a CC polymerization start from an initiator, which generated a dead chain end and an active end group. Thus, all growing steps result from reactions of monomers with the reactive end group. However, in contrast to normal ChainGPs, all growing steps of a CC polymerization are condensation reactions. **Scheme 8** illustrates a CC-polymerization for cyclic monomers



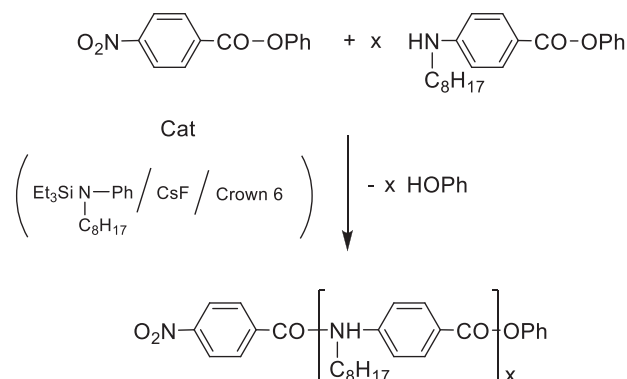
**Scheme 7.** Two-dimensional scheme of a segment of a multicyclic polymer.

( $\alpha$ -amino acid *N*-carboxyanhydrides)<sup>[26,27]</sup> and **Scheme 9** the CC-polymerization of a non-cyclic monomer (recently studied in much detail by Yokozawa et al.).<sup>[28]</sup> If a CC-polymerization exclusively proceeds by reaction of monomers with the initiated chain, the kinetic course, the definition of conversion and its correlation with the DP fully agree with those of a normal ChainGP (Equation (4)). However, CC-polymerizations of non-cyclic monomers have the tendency that monomers react with each other when the temperature is raised or when extremely high monomer/initiator ratios are used. In those situations, the Step GP begins to compete with CC-polymerization and difunctional chains having one “a” and one “b” end group are formed, which can react in three ways.

First, they can react with initiated chains and the polymerization continues like a normal CC-polymerization. Second, they can react with each other like a normal StepGP and third, they can cyclize. The detection of cyclic oligomers is, thus, a clear indication, that the entire polymerization process was not a clean CC-polymerization. For a proper description of such a complex polymerization two different definitions of conversion



**Scheme 8.** Ring-opening polymerization of  $\alpha$ -amino acid NCAs by initiation of primary amines; the first example of a CC-polymerization, published by H. Leuchs in 1907.<sup>[29]</sup>



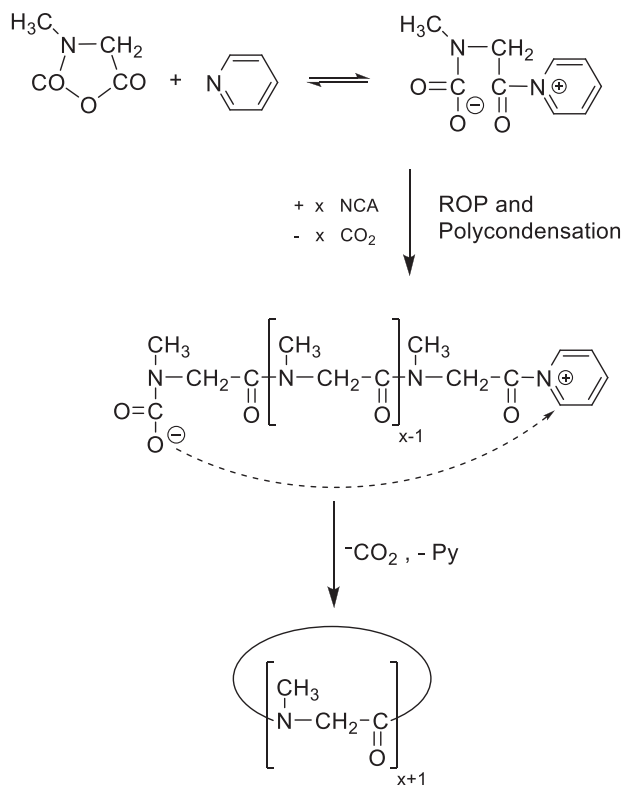
**Scheme 9.** CC-polymerization of a non-cyclic monomer.

are, in principle, necessary (Equations (4) and 6a,b)), but for preparative purposes it suffices to consider the consumption of monomers. Quantitative conversion may mean that the entire reaction product consists of initiator-terminated linear chains or that it consists of linear chains and cycles.

### 3.3.2. Ring-Opening Polymerization with Polycondensation (ROPPOC)

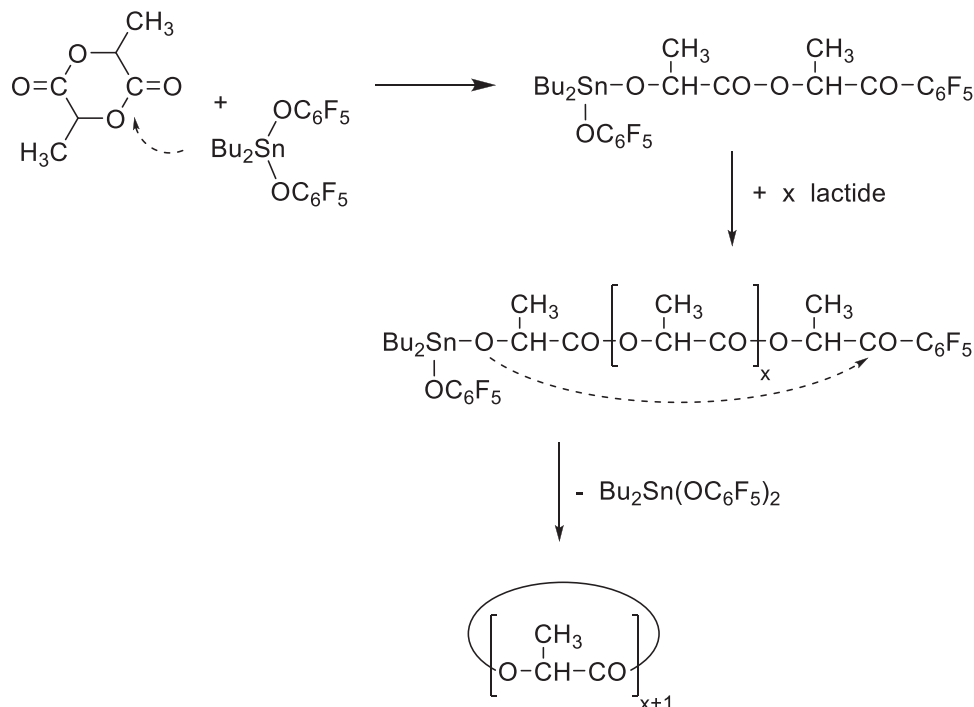
The second group of polymer syntheses combining ChainGPs and StepGPs will be called ROPPOC syntheses, meaning ring-opening polymerization combined with simultaneous polycondensation (for precise definition and reviews<sup>[30]</sup>). ROPPOC syntheses are particularly useful for the preparation of cyclic polymers, and numerous ROPPOC syntheses have been published over the past 15 years. Characteristic for the ROPPOC approach is that the initiator of the ROP generates a reactive and not a dead chain end. In this way difunctional chains are formed that do what all difunctional chains do in a normal StepGP, they continue chain growth by intermolecular condensation or they cyclize via intramolecular condensation.

Based on the covalent or ionic nature of the end groups, ROPPOCs may be subdivided into three categories. First, both chain ends are ions and the entire polymerization process is a zwitterionic polymerization as illustrated exemplarily in **Scheme 10**<sup>[31–33]</sup> Second, one chain end is covalent (e.g., an activated CO-group) and the other chain end is ionic (e.g. an anion). Third, both reactive end groups have a covalent character, as illustrated by the polymerization of lactides catalyzed by dibutyltin bisphenoxides (**Scheme 11**).<sup>[34]</sup> It should be emphasized that that identification of ROPPOC process via detection of cyclization requires absence of cyclization via “back-biting.” For example, in the case of polypeptides, polyamides, or aromatic polyethers the polymer backbone is too stable to undergo “back-biting” reactions. However, syntheses of polyesters may, in principle, involve “back-biting” even at room temperature. Yet, in the case of lactides the dimeric character has the consequence that a clean ROPPOC process yields even-numbered cycles and even-numbered linear chains, when cyclization is incomplete. The appearance of odd-numbered species indicates that transesterification reactions also occurred. These transesterification reactions are not in contradiction to the existence of a ROPPOC process, but they make its identification more difficult.



**Scheme 10.** Pyridine-catalyzed zwitterionic polymerization of sarcosine NCA.

Since the ROPPOC process consists of two different polymerization reactions two different definitions of conversion



**Scheme 11.** Ring-opening polymerization with simultaneous polycondensation (ROPPOC) of lactide by means of dibutyltin bis(pentafluorophenoxide).

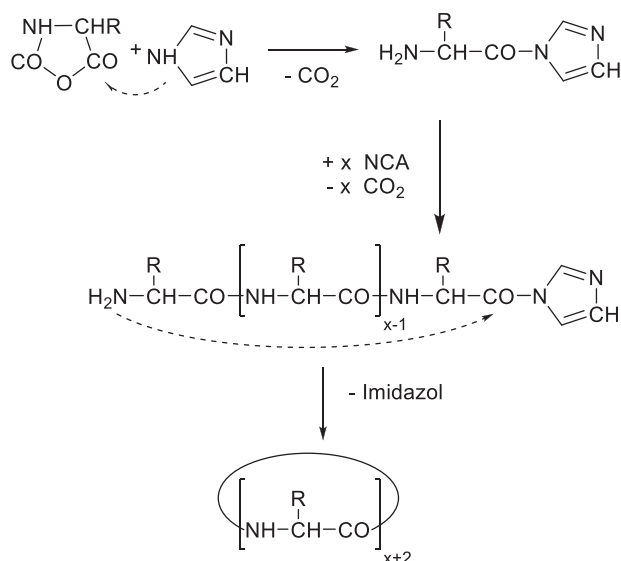
are needed for a proper description. For the ROP alone, definition (4) is adequate, like for any other ChainGP. Yet, for the condensation reactions Equation (6a,b), which are typical for any normal polycondensation, are not useful. In a normal polycondensation, the number of functional groups presents at the beginning ( $N_{f0}$ ) represents the maximum concentration of functional groups which decreases steadily with the conversion. However, in the ROPPOC case  $N_{f0}$  is zero. The number of functional groups passes then through a maximum and ends up with zero at 100% conversion. For such a process a modification of Equation (6), namely Equation (15) is required.

$$P = (N_{f1} - N_{f2}) / N_{f2} \quad (15)$$

With  $N_{f1} > 0$ : number of functional groups formed after partial reaction of catalyst with monomers at any arbitrary time  $t_1$ ;  $N_{f2}$ : number of functional groups at any time after  $t_1$ .

Two different scenarios were observed with regard to the extent of ROP and polycondensation/cyclization and to the definition of conversion. First, when all polymer chains stay in solution or in the melt, quantitative polymerization and cyclization are, in principle, possible. ROPPOC syntheses of cyclic polylactides by means of dibutyltin bis(pentafluorophenoxide) outlined in Scheme 11 may serve as an example for this scenario.<sup>[34]</sup> Second, it was observed in polymerizations of  $\alpha$ -amino acid NCAs that quantitative polymerization of the monomers was not followed by quantitative cyclization of oligomers and polymers. The oligopeptides of almost all natural amino acids can adopt the  $\beta$ -sheet structure which, due to intermolecular H-bonds, causes insolubility in all inert solvents useful for a clean polymerization of the NCAs.<sup>[31]</sup> When precipitation of the growing chains more is rapid than cyclization, linear





**Scheme 12.** Ring-opening polymerization with simultaneous polycondensation of amino acid N-carboxyanhydrides by means of imidazole.

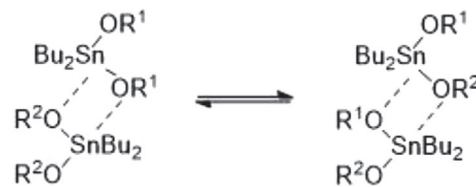
chains having two active end groups will be fixed in the  $\beta$ -sheet crystals and cyclization is prevented as long as these crystals exist. In the case of soluble  $\alpha$ -helix forming polypeptides (e.g., poly(benzyl- L-glutamate)) chain growth to  $DP$ s above 10 may result in the formation of  $\alpha$ -helices prior to cyclization.<sup>[31]</sup> The chain growth may continue at the end of the helices, but the helices are too stiff for cyclization. The CC-polymerization of  $\gamma$ -GluNCA initiated by imidazole (**Scheme 12**, In summary it may be said, that regardless, if the conversion of polycondensation/cyclization part of the ROPPOC process is complete or not, a simple correlation between conversion and DP does not exist.

## 4. Equilibration Reactions

### 4.1. Ring–Ring Equilibration

In principle, three kinds of equilibration reactions exist: ring–ring, ring–chain and chain–chain equilibration. Jacobson and Stockmayer<sup>[5,6]</sup> were the first who theoretically and experimentally explored such equilibration reactions with focus on ring–chain equilibria. As already mentioned by those authors, ring–chain equilibration automatically involves ring–ring and chain–chain equilibration. However, later polymerization processes were found involving chain–chain equilibration without formation of cycles or ring–ring equilibration without participation of linear chains.

Ring–ring equilibration may proceed by addition of a cyclic catalyst to a certain amount of a monodisperse ring (e.g., a cyclic monomer), or it may occur (in rare cases) spontaneously. For example, it has been demonstrated by NMR spectroscopy that tin alkoxides rapidly exchange alkoxide groups via donor–acceptor interactions (**Scheme 13**).<sup>[35]</sup> Therefore, cyclic tin alkoxides may undergo equilibration without needing an external catalyst. Other cyclic metal alkoxides having energetically favorable free d-orbitals may behave analogously. Regardless,



**Scheme 13.** Ligand exchange in dibutyltin bis-alkoxides via donor–acceptor interactions.

if an external catalyst is added or not, the monodisperse cycle used as starting material will not disappear, and a quantitative conversion in the sense of a total consumption of the monomer cannot be achieved. Furthermore, functional groups which change their structures, are not involved. Hence, neither Equation (4) nor Equation (6a,b) are adequate definitions of conversion.

From the view point of a cyclic monomer two scenarios may be envisaged. First, the equilibration starts out from the neat monomer or second, it starts out from a cyclic polymer and no monomer is present in the beginning. From the viewpoint of a cyclic monomer two scenarios may be envisaged. First, the equilibration starts out from the neat monomer and its concentration will decrease until the equilibrium concentration is reached. Second, the equilibration starts out from a large cycle or mixture of cyclic polymers and no cyclic monomer is present in the beginning, so that increasing conversion parallels its increasing concentration. In both cases the approach to the equilibrium concentration of the monomer may be considered as 100% conversion and the conversion may be defined by Equation (16). When the initial monomer concentration is neither 0 nor the maximum value of the neat monomer, but an intermediate concentration in between those extremes ( $C_{i1}$ ), Equation (17) may be applied. Concerning the DP of the reaction mixture three scenarios are possible. First, the average DP of the reaction mixture will increase, when the equilibration starts out from the neat monomer up to the equilibrium DP. Second, the same is true when the equilibration starts out from a mixture of cyclic oligomers or polymers, the average DP of which is lower than that of the equilibrated mixture. Third, when cyclic polymers with  $DP$ s higher than the equilibrium serve as starting materials, the average DP will, of course decrease with the ongoing equilibration:

$$p = (C_0 - C_p) / (C_0 - C_{eq}) \quad (16)$$

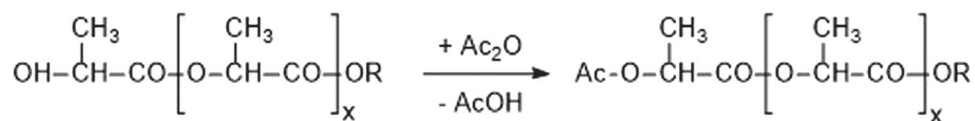
(with  $C_{eq}$  = monomer concentration at equilibrium, and  $C_p$  = monomer concentration at a given conversion)

$$p = (C_{i2} - C_{i1}) / (C_{eq} - C_{i1}) \quad (17)$$

with  $C_{i1}$  and  $C_{i2}$  = monomer concentration at time 1 or time 2.

### 4.2. Chain–Chain Equilibration

The above discussion of ring–ring equilibration has demonstrated that equilibration reactions need another definition of the conversion than polymer syntheses. Equilibration of



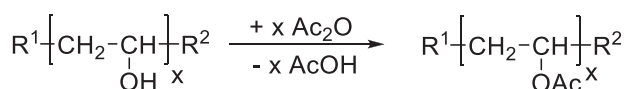
**Scheme 14.** Acetylation of OH-end groups.

linear chains frequently occurs in syntheses of polyesters, polycarbonates, and polyamides when these syntheses are performed at high temperatures (>200 °C) in the melt. These chain–chain equilibrations are accompanied by ring–chain and ring–ring equilibrations as discussed by Jacobson and Stockmayer. These equilibrations and their influence on the DP are directly related to the conversion and are not a separate phenomenon. However, in ROPs of lactones and lactides at temperatures below 160 °C chain–chain equilibration has been detected which proceed in the absence of back-biting and ring–chain equilibration. The role of intermolecular transesterification has theoretically and experimentally been studied in much detail.<sup>[36,37]</sup> Such transesterifications (or transamidations in the case of polyamides) do not change the average DP but may broaden the molecular weight distribution. The conversion of chains having an identical length ( $x$  in Equation (12)) may be defined by Equations (15 and 16) quite analogous to ring–ring equilibrations.

A special chain-chain equilibration was found for alcohol-initiated ROPs of L-lactide catalyzed by tin(II) 2-ethylhexanoate at temperatures below 130 °C, a catalyst system used for the technical production of polylactides.<sup>[38–42]</sup> This transesterification produces odd-numbered chains from the initially formed even-numbered ones by a selective exchange of only one lactic acid unit, so that no broadening of the molecular weight distribution curve takes place. Therefore this transesterification may be labeled single unit exchange mechanism (SEU). A plausible reaction mechanism has been published but not definitely proven yet.<sup>[43]</sup> When a single type of odd-numbered chains (with identical chain length  $x$ ) and its increasing concentration up to the equilibrium is considered, the conversion may also be defined according to Equation (15).

## 5. Chemical Modification of Polymers

A large number of chemical reactions have been published dealing with the chemical modification of polymers. The transformation of cellulose into its triacetate or nitrates are the oldest examples which played an important role in the history of polymer science.<sup>[42,43]</sup> These modification reactions may be subdivided into two categories, namely alterations of end groups (**Scheme 14**) and alterations of functional groups attached to repeat units in the polymer backbone (e.g., **Scheme 15**). Regardless which group of modifications is considered the conversion may be defined by the consumption of functional groups



**Scheme 15.** “Polymeranalogous” acetylation of poly(vinyl alcohol).

according to Equation (6a,b) quite analogous to the conversion of StepGPs. Clean modifications do not alter the molecular weight distribution, but they change the molar mass and this change is proportional to the conversion. Finally it should be noted that clean chemical modifications of functional groups in the repeat unit of various polymers (incl. biopolymers such as cellulose) played an important role in the history of polymer science. They allowed H. Staudinger to prove the existence of long polymer chains exclusively built up by covalent bonds, whereas polymers before 1930 were believed by almost all scientists to be associates of oligomers.<sup>[44]</sup>

## 6. Summary

This article discusses how the characteristic differences between the chemistry of small molecules and syntheses of polymers are reflected in understanding and definitions of the term “conversion.” In addition to what is known for a long time about chain GPs, various step-growth polymerizations and various equilibration and modification reactions were examined with respect to definition of conversion needed for a correct description of these reactions. Two aspects were in the focus. First, in contrast to the chemistry of small molecules, at least four different definitions of conversion are required to describe all kinds of reactions that may occur in polymer science: Equation (4) for chainGPs, Equation (6a,b) for stepGPs, Equation (15) for ROPPOCs, and Equation (16 and 17) for ring-ring equilibration. Second, it is shown for different classes of polymerization and modification reactions, how the extent of conversion may influence structure (e.g., end groups, chain length, branching), and/or topology (e.g., linear versus cyclic) of the resulting polymers.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

anionic polymerization, conversion, cyclization, equilibration, polycondensation, radical polymerization, ring-expansion polymerization

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