Competing exchange and irreversible reactions in a linear co-polycondensation lead to a broad composition window where tunable high molecular weight polymers can be prepared

Michael Lang$^{1*}$ and Frank Böhme$^{1}$

$^{1}$Leibniz-Institut für Polymerforschung Dresden, Hohe Straße 6, 01069 Dresden, Germany

A co-polycondensation reaction is discussed analytically and by Monte-Carlo simulations where two reactive units compete for reactions with an alternating third reactive unit, whereby irreversible reactions replace bonds which are able to undergo exchange reactions. The resulting number average molar mass, $M_n$, exhibits only one distinct peak at the stoichiometric condition of both competitors with the alternating partner. The weight average molar mass, $M_w$, reaches an additional second peak at the stoichiometric condition between the dominating competitor and the alternating partner. Both peaks of $M_w$ surround a range of compositions where a rather high and approximately constant $M_w$ is obtained. The degree of polymerization of the dominating and alternating reaction partners is rather insensitive towards composition fluctuations if the reaction mixture remains within this composition window. This promotes high molecular weight species and more homogeneous weight distributions at incomplete mixing conditions. An ideal reference case (identical reaction rates for all reactions) is solved analytically to describe these reactions. The position of the stable composition window and the average molar masses inside this window can be tuned by choosing appropriate precursor molecules, reaction mixtures or post-tuning steps at later times.
I. INTRODUCTION

Polycondensation is one of the basic classes of polymerization reactions that is typically covered in textbooks of polymer science [1, 2]. The basic principle of condensation reactions has been understood since the first half of the last century [3]. Later, developments focused mainly on the treatment of deviations from Flory’s ideality assumptions, which allowed to treat cyclization, substitution effect, or reactions in open systems [4]. Despite of the huge success made over the decades, the enormous amount of different reaction pathways, boundary conditions of the reactions, etc... still allows for discoveries both on experimental and theoretical side.

Current work at our institute [5] on the co-polycondensation (chain extension) of bisamino-terminated polyamide 12 (DD) with bisdithiooxalate (AB-CC-BA), see Figure 1, provides an example for such a particular situation. This co-polycondensation in the melt shows an extraordinary increase in molar mass over an unexpectedly wide range of compositions. This is largely surprising, as the key signature of a linear alternating co-polycondensation at complete reactions is the formation of a narrow peak in the average molar mass as a function of composition, see for instance equation (80) and (85) of the Appendix. In practice, cyclization reduces both the number and weight average degrees of polymerization [6, 7] and perfect mixing conditions becomes crucial for a stoichiometric ratio $r \approx 1$, since the average molar mass diverges there. Also, impurities or inactive groups may terminate a significant portion of the polymers. Most of these deviations from ideal reactions were worked out in numerous works that are summarized to some extent in Refs. [3, 4]. The general trend of these deviations is to cause a systematically lower degree of polymerization in the vicinity of $r \approx 1$. Therefore, these deviations cannot explain an extended range of compositions where high molecular mass products are available.

A closer inspection of the possible reactions in Ref. [5] indicates that the bisdithiooxalate contains four reactive centers that potentially react with the amino groups at the ends of the polyamide 12, see Figure 1. Reactions with the inner two of these reactive centers (B-C) result in the formation of an amide group and a hydroxy group. The two dithioester groups (A) at the ends of the bisdithiooxalate react with the amino or the hydroxy groups. These reactions form either a thioamide group (A-D) or a thioester group (A-C). Since reactions with the inner reactive centers cut the bisdithiooxalate in two parts, only linear molecules result from these reactions.

With this reaction scheme in mind, one is prompted directly to generalizations of the alternating polycondensation reaction scheme where two different reaction partners CC and DD compete for
Figure 1. Top: bisdithiooxalate and amino terminated polyamide 12. Bottom: scheme of possible reactions. Taken from ref. [5].

reactions with a third reaction partner AB but do not react with one another. The expected behavior of such a reaction is quite obvious: as long as the AB moieties are in the majority with respect to the sum of CC and DD moieties, all CC and DD moieties will be incorporated into the chains and reaction rates affect only the sequence of CC and DD between the AB moieties. If the AB moieties become minority, the reaction rates will control how many CC and DD moieties can be found inside the chains that contain AB moieties and how many of these remain non-reacted.

Such a line of arguments could be used for irreversible reactions and a numerical solution can be obtained by integrating over the reaction rates or running rate dependent Monte Carlo simulations, see section II and III below. However, we have to emphasize that the amide and the thioamide groups are stable, while the thioester and ester groups may undergo further reactions with hydroxy or amino groups. In effect, the amino group can displace the bound hydroxy groups. The hydroxy
groups themselves undergo an alcoholysis reaction that leads to a bond exchange similar to a transesterification, see reactions (v)-(vii) in Figure 1. Thus, from a general point of view, we discuss two kinds of competing reactions, one is irreversible and the second one is an exchange reaction that forms a special kind of a “reversible” bond where the density of bonds is controlled by stoichiometry. We argue that this situation refers to the competition of moieties CC and DD for bonds with AB, where DD dominates over the competitor CC in such a way that the CC moieties effectively react merely with the “leftover” reactive groups after the coupling of AB with DD. This point is demonstrated in our work by the excellent agreement of Monte-Carlo simulation that reproduces the full reaction scheme of Figure 1 on one side, with analytical computations on the other side that consider such a dominance of DD moieties over CC moieties.

The formation of reversible bonds or “supramolecular polymerization” \cite{8, 9} itself is well understood, in particular for equilibrium systems \cite{10–13}. Indeed, even the competition between cyclization and linear polymerization is solved (up to some minor details) for these systems in contrast to irreversible polymerizations, where the history of reactions impacts the resulting weight distributions \cite{3, 7}. However, despite the large body of work on reversible and irreversible polycondensation in general (see, for instance, Refs \cite{3, 4} for a review), the authors could not find examples of competing reversible and irreversible (or exchange) reactions within a linear condensation co-polycondensation. Also, specialized works where CC and DD react with AB \cite{14}, publications on chain extension \cite{15–18}, exchange reactions (transesterification, acidolysis, alcoholysis, ...) \cite{19–21}, and competing irreversible reactions \cite{22}, or simulations works that model forward and backward reactions \cite{23}, did not provide models that may enable a quantitative discussion of the experimental data of Ref. \cite{5}.

This gap is closed with the present work. We first introduce a mean field kinetic model that describes all possible reactions of Figure 1 in section II. Afterwards, we develop a Monte-Carlo model that resembles the reactions of the kinetic model in order to capture the main aspects of the polycondensation reaction in section III. These simulations indicate that the reaction products are not much sensitive to reaction rates for our model case as discussed in section V A. Therefore, statistical arguments are used in section IV for the “equireactive” case (all reaction rates are identical) to derive analytical expressions for the number and weight average molar mass of the reaction products. The Monte-Carlo simulations allow to compute the molar mass distribution of the full sample \cite{24, 25} and specific weight distributions of particular moieties can be analyzed. We use these to derive moiety specific degrees of polymerization as molecules with or without
a particular type of moiety may be separated out of the reaction bath or may dominate the molar mass as in Ref. [5]. One particularly interesting point of our results is that a “dominated co-polycondensation” provides a range of compositions, where the average molar mass of some reaction products is rather independent of composition. How this composition range can be tuned and how average molar masses or specific degrees of polymerization can be adjusted ex posteriort is discussed in section V.

II. KINETIC MODEL

The kinetic equations that describe the reaction scheme of Figure I can be written as follows for all reactive groups A, C, and D and all bonds A-D, A-C, B-C, and B-D, whereby bonds containing C groups may undergo further reactions:

\[
\frac{d[A]}{dt} = -k_a[A][D] - k_c[A][C]
\]  

\[
\frac{d[C]}{dt} = k_b[B-C][D] + k_d[A-C][D] - k_c[A][C]
\]  

\[
\frac{d[D]}{dt} = -k_a[A][D] - k_b[B-C][D] - k_d[A-C][D]
\]  

\[
\frac{d[A-C]}{dt} = k_c[A][C] - k_d[A-C][D]
\]  

\[
\frac{d[A-D]}{dt} = k_a[A][D] + k_d[A-C][D]
\]  

\[
\frac{d[B-C]}{dt} = -k_b[B-C][D]
\]  

\[
\frac{d[B-D]}{dt} = k_b[B-C][D]
\].

The equations above reflect only reactions (i-iv) of the reaction scheme, Figure I, which change the concentrations of the reactive groups or bonds. The alcoholysis reaction does not affect the concentration of bonds or reactive groups, but rearranges structure as indicated by reactions (v)-(vii) in Figure I. These need to be considered additionally for the Monte-Carlo simulations.

We further denote by \([P]_0\) the initial concentration of the bisdithiooxalate molecules. As stoichiometric ratio \(r\) we define the ratio of reactive D groups with respect to the reactive groups on
AB moieties,

\[ r = \frac{[D]}{4[P]_0} = \frac{[D]}{[A] + [B]}. \]  

The coupled set of differential equations, equation (1)-(7) was integrated numerically. The resulting concentrations of all reactive groups and bonds were used to double check the corresponding results of the Monte-Carlo simulations. We obtain that the final conversion of A, C or D depends solely on the stoichiometric ratio \( r \) and not on reaction rates:

- For \( r < 1/2 \), a portion of \( 1 - 2r \) of the A groups remain non-reacted, while all C and D groups are bound.
- For \( 1/2 < r < 1 \), a portion of \( 2r - 1 \) of the C groups are not bound to other groups, while all A and D groups are bound.
- For \( r > 1 \), a portion of \( 1 - 1/r \) of the D groups is not reacted, while all A groups are bound and all C moieties are not bound and belong to non-reacted moieties CC.

In consequence, the number average degree of polymerization, \( N_n \), depends solely on \( r \) and not on reaction rates as \( N_n \) is determined only by the concentration of chain ends (unbound A, C, and D groups). However, such arguments do not apply for higher order averages like weight averages or for specific degrees of polymerization where averages over one type of moiety are performed, as these depend on the corresponding weight distributions and thus, must depend on reaction rates. This can be seen also from the numerical solution of the rate equations, as the frequency of bonds that are formed is indeed a function of the reaction rates.

Explicit variation of individual reaction rates by one order of magnitude up or down shows only a weak impact on \( N_w \) as discussed in section [V.A]. As it will turn out below, a dependence on reaction rates is only possible when moieties with different reactive groups on both ends are involved or initially some groups are already reacted, which is not the most typical situation for chain extension. Therefore, we focus in the following sections on the case of an equal reactivity of all groups (as in similar work, e.g. [27, 28]), moieties with identical reactive groups on both ends, and initially unconnected moieties to derive a simple analytical approximation. Similar to these works, we ignore also the formation of cyclic molecules. This leads to a slight overestimation of the molar mass [7] as most cyclic species are rather short and consist of a stoichiometric amount of moieties for our alternating co-polycondensation. This leads in effect to a higher density of
the majority units (i.e. chain ends) on the linear species, which reduces additionally the average molar mass of the linear chains.

III. MONTE-CARLO SIMULATIONS

The bisdithiooxalate molecules are modeled by a sequence of three moieties AB-CC-BA connected by two B-C bonds, see top of Figure [1]. DD moieties are modeled by single unconnected moiety at the beginning of the simulations. A large number of $Z$ bisdithiooxalate molecules, $10^5 \leq Z \leq 10^6$, are reacted with an amount $rZ$ of polyamide 12 within a Monte-Carlo scheme that resembles the reaction scheme of Figure [1]. All non-reacted A, C, and D groups and all B-C and A-C bonds are considered as reactive units, see section [II]. Reaction rates $k_i$, $i = a, ..., d$ were normalized with respect to the largest reaction rate $k_{\text{max}}$ among these, such that we can define acceptance rates $p_i$ for particular reactions through

$$p_i = \frac{k_i}{k_{\text{max}}}$$

where the $i = a, ..., g$ indicates the reaction rates according to the reaction scheme in Figure [1].

The Monte-Carlo scheme runs as follows:

1. Select randomly a pair of reactive groups.

2. Check whether these pair of groups can undergo a reaction (C or D must react with A, A-C, or B-C). If not, return to step 1.

3. Accept possible reactions with probability $p_i$. If rejected, return to step 1.

4. Perform reaction and update connectivity table and list of reactive groups.

5. Repeat steps 1-4 until either no more groups are reactive on DD moieties (for $r < 1$), or all A and B groups are reacted with D groups (for $r > 1$).

6. For $r < 1$: further equilibrate structure by additional reactions of type (v)-(vii) in Figure [1] such that at least 5 interchange reactions were performed per reactive C group.

The first two steps assure that reactions occur proportional to the concentrations of reactive groups. Effectively, a random selection of reaction partners suppresses also cycle formation because of the large numbers of molecules used. For our simulation parameters with a number of $Z_0 \geq 10^5$
molecules at the start and $Z_1 \geq 10^3$ at the end (we do not approach critical points closer than 1% of conversion), the expected total number of rings formed is estimated by summation over all ring closure probabilities, $\sum_{i=1}^{Z_0} 1/(2i-1) \leq 2.4$. The resulting number fraction $< 0.0024$ is too small to cause visible deviations between simulation data and theoretical predictions. Nevertheless, we also detected size of rings and considered them as linear chains of same weight for the numerical analysis to further reduce the difference between theory and simulation data.

Step 3 of the above scheme controls that the frequency of reactions occurs with correct relative rates. For step 4 one has to be aware that any reaction with an existing bond transfers the reactivity label to the previously bound C group. Steps 5 and 6 control the end of the reactions and allow for possible structural rearrangements (for $r < 1$) to drive the sample to equilibrium.

The above simulation scheme provides connectivity tables of all molecules. These connectivity tables were used to determine the number and weight average degrees of polymerization with respect to either all moieties or a selected type of moiety. The results of this analysis for the equireactive case are used as a reference for our analytical discussion in the following sections. We also ran simulations with different reaction rates to get an insight into the impact of different reaction rates on the average molar mass. These results are discussed in section IV A.

**IV. ANALYTICAL SOLUTION OF THE EQUIREACTIVE CASE**

**A. General Remarks**

In the Appendix, we include a derivation of average and specific degree of polymerization and the weight distributions for the simplest case of an ideal alternating polycondensation of two monomers. This case is included as a reference system and the scheme of derivation there serves as a blueprint for the more complex situation of Figure 1 discussed below.

We have to point out that the initial condition of the reaction mixture of ref. [5] introduces a non-random sequence of moieties, since initially, all C groups are attached to B groups. Alcoholysis helps to approach the random limit, as the bonds containing a C group are continuously regrouped. But the bonds with D groups are stable and thus, still “memorize” the conditions during bond formation. In fact, the initial condition of 100% of C-B and no A-C bonds refers to a maximum possible deviation between experimental data and the analytical solution that is derived for the simplest “equireactive case” where all reaction rates of Figure 1 are identical. As we shall
see below, these differences are not very large, which provides a strong argument in favor of using our analytical solution as a reasonable approximation.

Below, we simplify the declaration of the structural units in the top part of Figure 1 and consider only two-functional moieties of type A (the alternating partner), C (the competitor), and D (the dominator). Thus, the equivalent initial set up to Ref. [5] consists of a mixture of three connected A-C-A moieties and isolated D moieties. We further generalize our discussions by allowing for different ratios $s$ of C moieties with respect to A moieties

$$s = \frac{[C]}{[A]},$$

(10)

while we keep the same variable $r$ for the ratio of reactive groups on D moieties with respect to former AB (now A) moieties

$$r = \frac{[D]}{[A]}.$$  

(11)

To simplify the derivation, we further introduce a portion $b$ of bound groups of the species that terminates chains. In general, the special solution for $s = 1/2$ presented below refers to the situation of Ref. [5]. However, additional corrections are necessary for $r < 1 - s$ to approximate the effects that arise from the non-random sequence of bonds that are caused by the specific initial conditions used in Ref. [5].

From a practical point of view, it might be interesting to know the “specific degree of polymerization” $z_X$ with $X = A, C, D$ that provides the average number of $X$ moieties in chains that contain at least one moiety $X$. Note that the reactions in the following sections may form polymers where not all three types of moieties are present; such polymers may phase separate from the reaction mixture or may be taken out from the mixture by a chemistry specific separation technique such as interaction chromatography. In the special case of Ref. [5], there is one moiety much larger than the rest such the specific degree of polymerization of this unit dominates the reaction mixture. In such a case, the average molar mass is less suitable to characterize the mixture [26]. Note that we use here a symbol $z$ and $z_X$ instead of $N$, or $N_X$ for the number average degree of polymerization and the specific degrees of polymerization with respect to moieties, since the moieties must not consist of single monomers. This is also the case in Ref. [5] where the moiety DD refers to polyamide 12.

Note that number and weight averages molar masses $M_n$ and $M_w$ might be available from Ref. [27, 28] in some cases by a simplification of some more general results. However, the specific average degrees of polymerization $z_X$ have not been computed previously. Since one can derive
$M_n$ and $M_w$ through $z_X$, we follow this route and double check thereafter whether the average molar masses agree with previous results, whenever these are available.

### B. D-terminated Chains: $[D] > [A]$

We start with the simplest case of D-terminated chains, since here, all C moieties are isolated at the end of the reactions,

$$z_C = 1,$$  

(12)

see section III. Note that this refers in Ref. [5] to the case of $r > 1$. We start with considering an ideal alternating polycondensation of A and D moieties. Here, the D units are in the majority with respect to A units such that we introduce a fraction of bound D groups (i.e. conversion of D groups)

$$b = \frac{[A]}{[D]} = \frac{1}{r}$$  

(13)

to map the problem on the solution presented in the Appendix. Then, $1 - b$ is the probability that a given D group terminates a chain made of A and D moieties or non-reacted D moieties. With the results of the Appendix we obtain that both specific degrees of polymerization are identical

$$z_D = \frac{1}{1 - b} = \frac{r}{r - 1} = z_A,$$  

(14)

even though each polymer contains one more D moieties than A moiety. The reason for the above equivalence is that the non-reacted D moieties do not contribute to $z_A$, see equation (88) of the Appendix. However, the non-reacted D moieties contribute to the total number of moieties in AD polymers, $z_{AD}$. Since there is always one A moiety less than D moieties for each chain, we obtain

$$z_{AD} = 2z_D - 1 = \frac{1 + b}{1 - b} = \frac{r + 1}{r - 1},$$  

(15)

which is the classical result for a strictly alternating copolymerization, see equation (80) of the Appendix.

Let us introduce $M_A$, $M_C$ and $M_D$ to denote the molar mass of an A, C, and D moiety respectively. A portion of $1 - b$ of all chains are non-reacted D moieties, while the remaining chains have one more D moiety than A moieties. Thus, the D containing chains have a number average molar mass of

$$M_{n,AD} = b (z_A M_A + (z_A + 1) M_D) + (1 - b) M_D =$$
There are $r/(zDs)$ chains with $z_D$ moieties D per isolated moiety C with $z_C = 1$ moieties C. This results in an average number of moieties per chain of

$$z = \left( \frac{r/(zDs)}{r/(zDs) + 1} \right) z_{AD} + \frac{1}{r/(zDs) + 1} z_C$$

$$= \frac{s + r + 1}{s + r - 1}.$$

The most interesting point of this result is that the average number of moieties per molecule, $z$, diverges at a critical composition of

$$r_c = 1 - s,$$

which is at a different position than the critical points of the specific degrees of polymerization $z_D$ and $z_A$, which diverge at

$$r_c = 1.$$

This is qualitatively different to an irreversible alternating co-polycondensation, where all degrees of polymerization (specific & average) diverge at the same critical point (cf. with the Appendix).

Let us introduce the composition average molar mass per moiety:

$$\overline{M} = \frac{M_A + sM_C + rM_D}{r + s + 1}.$$  

With this definition, one obtains for the number average molar mass of all molecules that

$$M_n = \frac{(r - 1) M_{n,AD}}{r - 1 + s} + \frac{sM_C}{r - 1 + s}$$

$$= \frac{M_A + sM_C + rM_D}{r - 1 + s} = z\overline{M}.$$  

All results of this section are exact and confirmed by simulation data, see Figure 2 where the predictions above are double checked with Monte-Carlo simulation data.

The termination argument used to derive equation (14) indicates that the weight distribution of $z_A$ and $z_D$ are most probable ones. The number fraction distribution, $n_N$, of chains containing either $N$ moieties A or $N$ moieties D (among all chains containing at least one A or at least one D moiety) are identical and of most probable type:

$$n_{N,A} = n_{N,D} = (1 - b) b^{N-1} = (r - 1) r^{-N}.$$
Figure 2. Average degrees of polymerization for $r > 1$ and $s = 1/2$ (specific case of Ref. [5]). Comparison of Monte-Carlo simulation data (data points) and the corresponding analytical solutions for the equireactive case (all reaction rates are identical) as given in the text and shown by the lines.

This leads to a polydispersity of [2]

$$\frac{z_{w,A}}{z_A} = \frac{z_{w,D}}{z_D} = 1 + b = \frac{r+1}{r},$$

(23)

since $b$ is the fraction of reacted groups that connect to another molecule, i.e. it is equivalent to conversion for the classical case of polycondensation of a single type of monomer. Therefore,

$$z_{w,A} = z_{w,D} = \frac{1+b}{1-b} = \frac{r+1}{r-1} = z_{AD}.$$  

(24)

The weight average molar mass of the whole sample is obtained by averaging (according to the corresponding weight fractions) the weight averages of independent distributions (distribution of $C$ moieties is independent of the combined $AD$ distribution). The molar mass of a chain containing $N-1$ moieties of type A and $N$ moieties of type D is

$$M_{N,AD} = (N-1)M_A + NM_D.$$  

(25)
The weight average molar mass of all D containing chains is then computed using the first and the second moment, $m_1$ and $m_2$ of the number fraction distribution

$$M_{w, AD} = \frac{m_2}{m_1} = \frac{\sum_{N=1}^{\infty} n_{N, AD} M_{N, AD}^2}{M_{n, AD}}$$

$$= \frac{(b + b^2) M_A^2 + (1 + b) M_D^2 + 4bM_A M_D}{(1 - b) (bM_A + M)}.$$  

$$= \frac{(r + 1) M_A^2 + (r^2 + r) M_D^2 + 4rM_A M_D}{(r - 1) (M_A + r M_D)}.$$

This result agrees with a simplified version of equation (3) of Ref. [27] (see also corrections to Ref. [27]). By setting $M_A = M_D = 1$ we obtain the weight average number of moieties in the D containing chains

$$z_{w, AD} = \frac{b^2 + 6b + 1}{1 - b^2} = \frac{r^2 + 6r + 1}{r^2 - 1}.$$  

(27)

Note that this result was obtained directly in the Appendix, equation (85), and is the classical result for a strictly alternating linear polycondensation. Note that the corresponding polydispersity approaches 2 for $r \to 1$ similar to an ideal condensation polymerization, but with a different function, see Figure 3 and equation (86).

In order to obtain $M_w$ and $z_w$ of the full sample, we have to combine $M_{w, AD}$ with $M_{w, C} = 1$ with respect to their weight fractions within the sample. There is a number fraction of $s/(1 + r + s)$ C moieties in the sample. Thus, the weight fraction

$$w_C = \left( \frac{s}{1 + r + s} \right) \frac{M_C}{M}$$

of C moieties in the sample is combined with the above results for $M_{w, AD}$ and $w_C$ to provide

$$M_w = (1 - w_C) M_{w, AD} + w_C M_C.$$  

(29)

For $M_A = M_C = M_D = 1$, the resulting expression can be simplified to

$$z_w = \frac{r^2 + 6r + sr - s + 1}{(r - 1) (1 + r + s)}.$$  

(30)

The corresponding polydispersity is here

$$\frac{z_w}{z} = \frac{(r^2 + 6r + sr - s + 1) (r + s - 1)}{(r - 1) (1 + r + s)^2}.$$  

(31)
which diverges for $r \to 1$, since $z_w$ diverges, while $z$ remains finite (see also Figure 2). This is a rather unusual behavior for a linear condensation polymerization, where usually both averages diverge at the critical point while the polydispersity remains finite. In our case, the divergence is caused by the presence of a large number of C moieties that are expelled from the chains and that keep $z$ finite. This situation is qualitatively similar to a non-linear poly-condensation where the abundant sol molecules prevent the number average molar mass from divergence at the gel point. The main results of the analytical derivation above were double checked with simulation data showing perfect match between both, see Figure 3.
C. A-terminated Chains: $[A] > [C] + [D]$

Since the number of A moieties is larger than the number of C and D moieties for this case, all chain ends are established by A moieties, see section II. Thus, all C and D moieties are completely reacted at full conversion and serve as bonds between A moieties. Note that this case is equivalent to the condition $r + s < 1$, which refers for $s = 1/2$ to the case $r < 1/2$ in Ref. [5]. For this limiting case, there are significant correlations due to the special chemistry of Ref. [5], which starts from a non-random sequence of moieties where the A moieties have two different reactive sites at their ends. This non-randomness affects higher order averages of molar mass and some specific averages, but it must disappear from the distribution in the limit $r \to 1$ where all “initial” bonds with C moieties are replaced by new bonds with D moieties. Therefore, we have to specify our results for the random case further to apply these to the particular situation of Ref. [5].

The most intuitive way to derive the general solution of the random case is by using a probability $b$ that describes the density of bound groups of the majority A moieties (i.e. the conversion of A groups)

$$b = \frac{[C] + [D]}{[A]} = s + r, \quad (32)$$

and the mixture of C and D moieties by a probability $p$ that a “bond” between A moieties is a D moiety:

$$p = \frac{[D]}{[D] + [C]} = \frac{r}{r + s}. \quad (33)$$

There are in average

$$z_A = \frac{1}{1 - b} = \frac{1}{1 - s - r} \quad (34)$$

A moieties per chain. The number of “bond” moieties (C or D) is always one less: $z_A - 1$. Thus, the average number of moieties per chain is

$$z = 2z_A - 1 = \frac{1 + b}{1 - b} = \frac{1 + s + r}{1 - s - r}. \quad (35)$$

The average molar mass of a chain inside the reaction mixture is computed by considering $p$ to split the portion of connecting moieties into C and D type. Using the above results we obtain for the number average molar mass, $M_n$, that

$$M_n = z_A M_A + (z_A - 1) \left( p M_D + (1 - p) M_C \right) \quad (36)$$

$$= \frac{M_A + r M_D + s M_C}{1 - s - r} = \bar{M}. \quad (37)$$
For deriving $z_D$ and $z_C$, we assume a random sequence of C and D along all chains. For computing $z_D$, we need to leave aside all chains that are entirely connected by C units and vice versa. As in the above section, we make use of the point that the number fraction distribution of a sequence of $N \geq 1$ “bonds” is equivalent to the most probable number fraction distribution, $n_N$, of a chain containing $N$ units, which is terminated with probability $1-b$ that a connection is missing,

$$n_N = (1-b) b^{N-1} = (1-s-r)(s+r)^{N-1}.$$  \hfill (37)

The probability that a sequence of $N$ connecting groups is of type C is $(1-p)^N$. The total number fraction of chains that contain exactly $N$ moieties of type C (and thus no D moiety) is therefore

$$n_{N,C} = \sum_{N=1}^{\infty} n_N (1-p)^N = \frac{1-b}{b} \sum_{N=1}^{\infty} (b(1-p))^N
= \frac{1-s-r}{s+r} \sum_{N=1}^{\infty} s^N = \frac{(1-s-r)s}{(s+r)(1-s)}. \hfill (38)$$

Recall from the case $r > 1$ that the specific degree of polymerization of the minority species is the same as the specific degree of polymerization of the majority moieties, see equation (14). Thus, the average number of D moieties per all molecules is the average number of C and D moieties per molecule times $p$, which gives $z_A p$. These D moieties, however, are only located on the number fraction of $1-n_{NC}$ chains that contain at least one D moiety. This increases the average number of D moieties per D containing chain, $z_D$, from $z_A p$ to

$$z_D = \frac{z_A p}{1-n_{N,C}} = \frac{1-s}{1-s-r}. \hfill (39)$$

With similar arguments, one obtains the number fraction of bond chains containing exactly N moieties D

$$n_{N,D} = \frac{1-b}{b} \sum_{N=1}^{\infty} (pb)^N = \frac{(1-s-r)r}{(s+r)(1-r)}. \hfill (40)$$

which leads to

$$z_C = \frac{z_A (1-p)}{1-n_{N,D}} = \frac{1-r}{1-r-s}. \hfill (41)$$

As before, our results are checked against simulation data, here for the equiractive random case (no initial B-C bonds), see Figure 4.

In contrast to the random case, the situation in Ref. 5 enforces $z_C = 1$ at $r = 0$ instead of $z_C = 2$. Furthermore, correlations among the sequence of C and D moieties are introduced through the different ends of the A moieties. These survive in part from the enforced initial conditions and
Figure 4. Degrees of polymerization from Monte-Carlo simulations (symbols) of the random case as compared to the model predictions for $r < 1 - s$ with $s = 1/2$, which are shown with lines.

are introduced to some other part through different reaction rates of C and D with the different ends of A. The third principal difference to the random case is, that at $r = 0$ despite of $s > 0$ all A moieties are chain ends.

As obvious from the above derivation, $M_n$, $z$, and $z_A$ depend only on the density of ends and not on the sequence of bonds - in contrast to $z_C$ and $z_D$. Therefore, the above results for $M_n$, $z$, and $z_A$ hold also for the simulation data that resemble the situation of Ref. [5]. A simple zero order approximation for $z_C$ and $z_D$ in Ref. [5] is to consider that the initial conditions were equivalent to the polycondensation of A-C-A unit with D moieties (assuming no exchange of bonds with C moieties). Then, simply,

$$z_C = \frac{z_A}{2} = z_D,$$

whereby the last equivalence is inferred from the results for the two partners of an ideal polycondensation (in the above simplification, D and C moieties are alternating along the chains), see the Appendix.
Figure 5. Degrees of polymerization from Monte-Carlo simulations (symbols) that resemble the special conditions of Ref. [5] for \( r < 1 - s \) with \( s = 1/2 \) compared with theoretical predictions. The thick black line indicates the simple approximation, equation (42), while the lines for \( z_C \) and \( z_D \) indicate the exact solutions mentioned below equation (42).

A comparison with the Monte-Carlo simulation data in Figure 5 shows perfect agreement of the theoretical predictions with \( z \) and \( z_A \) of the majority species for simulations, that resemble the equireactive case with initial conditions as in Ref. [5] (A-C-A initial sequence of all A and C moieties). The data for the minority species, \( z_D \) and \( z_C \), are close to the simple approximation of equation (42). A more detailed discussion of the correlations introduced by initial conditions and propagated by the asymmetry of AB moieties (not included here) shows, that the solutions for the special case of Ref. [5] are shifted with respect to the simple approximation by \( \pm (r/2 + r^2) \) in the equireactive case, see also Figure 5. Since this shift is still in the range of a 10\% correction, we argue that a simplification similar to equation (42) should provide a reasonable approximation for \( z_C \) and \( z_D \) of the minority species in similar cases.

Let us now return to the random case of equally reactive groups. For the derivation of the
weight averages, we make use of the findings for $r > 1$ and of the derivation in the Appendix. First, all specific “degrees of polymerization” $z_X$ with $X = A, C, D$ are characterized by a most probable number fraction distribution, see the above derivation. Therefore, the polydispersity of these special degrees of polymerization $z_X$ is the same as for a most probable distribution as a function of the average degree of polymerization, see also equation (90) of Appendix. This provides directly

$$z_{w,A} = z_A (1 + b) = \frac{1 + s + r}{1 - s - r} = z,$$

(43)

$$z_{w,C} = z_C (1 + b) = (1 - r) z,$$

(44)

$$z_{w,D} = z_D (1 + b) = (1 - s) z.$$

(45)

Similarly, the average number of moieties per chain must be characterized by the polydispersity of an ideal co-polycondensation, since the A moieties form a perfectly alternating sequence with the remaining moieties. Using equation (86) of the Appendix we arrive at

$$z_w = z \frac{1 + 6b + b^2}{(1 + b)^2} = \frac{1 + 6(r + s) + (r + s)^2}{(1 - r - s)(1 + r + s)}.$$

(46)

These results are tested by comparing the polydispersities of the different cases with simulation data in Figure 6.

For the special situation of Ref. [5], we adopt the same simple approximation as above and interpret the initial conditions as a polycondensation of A-C-A unit with D moieties without re-grouping of bonds with C moieties. Thus, we expect that all specific degrees of polymerization show the polydispersity of a most probable distribution. The only necessary correction is to renormalise $z_A$ by a factor of 1/2 to take into account that each A-C-A unit contributes two A moieties. Similarly, we scale $z$ down by a factor of

$$z_0 = \frac{3 + 2r}{1 + 2r},$$

(47)

which is the average degree of polymerization at the onset of the reactions. Figure 7 shows that our expectation is fully satisfied for $z_C$ and $z_D$ while the simple re-scaling leads to less satisfactory results for $z$ and $z_A$ where polydispersity is clearly overestimated. Still, the error for $z_A$ is in the range of 10%, while for the special situation of Ref. [5] the polydispersity of a polycondensation might be taken as a reference for the re-scaled $z_w$ instead of the expected co-polycondensation case. The reason for the lower polydispersity is the suppression of species that contain only single moieties at intermediate degrees of polymerization, which leads to a consecutive suppression of
Figure 6. Polydispersity for $r < 1 - s$ and $s = 1/2$ plotted as a function of the average degree of polymerization. While all specific degree of polymerization $z_X$, $X = A, C, D$ are of most probable type, see equations (43)-(45), $z$ is of an ideal alternating polycondensation type, see equation (46).

Therefore, we expect the data of the experiments of Ref. [5] in the vicinity of

$$z_w \approx z(1 + b) = \frac{(1 + r + s)^2}{1 - r - s},$$

and similarly, we approximate

$$M_w \approx M_n (1 + b) \approx z_w \overline{M}.$$  

D. C-terminated Chains: $[D] < [A] < [C] + [D]$

In this section, we combine the results of the preceding two sections, as both critical points at the boundaries control the average degrees of polymerization. A comparison of our simulation data
Figure 7. Polydispersity as a function of $z$ (note the re-normalization of $z_A$ and $z$ discussed around equation (47)) for the specific situation of ref. [5] with $s = 1/2$.

for the random case and the one with initial conditions as in Ref. [5] shows that the correlations from initial conditions can be ignored here. The physical explanation for this observation is that the C moieties, which carry the correlation to the initial conditions, are increasingly expelled from the chains with increasing $[D]$ such that initial correlations or the effect of a different reactivity become negligible for $r \rightarrow 1$. Since the degrees of polymerizations are typically $\gg 1$ for this section, the remaining small correlations are averaged out to a large extent. Therefore, we derive here the solutions for the random case and compare directly with data for the specific simulations that resemble the situation of Ref. [5] for the case $1 - s < r < 1$. Agreement between both supports the proposal that correlations can be ignored.

Let

$$b = \frac{[A] - [D]}{[C]} = \frac{1 - r}{s}$$

(50)

denote the fraction of the bound C groups with respect to all C groups. Since $1 - b$ defines the probability that a C group terminates a chain of C units (leaving aside the completely reacted A
and D moieties in between), we have

\[ z_C = \frac{1}{1 - b} = \frac{s}{s + r - 1}. \]  

(51)

Again, a fraction of \(1 - b\) of all chains are isolated C moieties. Thus, all A moieties are distributed only among a portion \(b\) of chains. Since there are in average \(1/s\) moieties A per C moiety, we have

\[ z_A = \frac{z_C}{sb} = \frac{s}{(1 - r)(s + r - 1)}. \]  

(52)

Similar to the preceding cases, the distribution of \(z_A\) is of an ideal condensation polymerization type, however, there are now two critical points that control \(z_A\) as indicated by the denominator of equation (52). But since the C moieties are expelled from the chains at \(r = 1\), there is only one critical point for \(z_C\).

The average degree of polymerization, \(z\), has here two contributions: one from the chains containing A moieties and one from the isolated C moieties. The number fraction of isolated C moieties among all chains is \(1 - b\), while the fraction of longer chains is \(b\). The average number of moieties on the A containing chains is \(2z_A + 1\), since A is minority here. Thus,

\[ z = b(2z_A + 1) + (1 - b) \]

\[ = \frac{r + s + 1}{r + s - 1}. \]  

(53)

In order to compute \(z_D\), we have to compute the probability \(p_j\) that an inner “bond” connecting two A moieties is of type D. The weight fraction of C moieties that are not an end is \(b^2\). Therefore, there is a portion of

\[ p_j = \frac{r}{b^2s + r} = \frac{rs}{(1 - r)^2 + rs} \]  

(54)

inner bonds that are of type D. Let

\[ t = \frac{1}{z_A} \]  

(55)

denote the probability per A moiety that a “chain” of A moieties is terminated by an excess C moiety. Again, the same number fraction distribution applies for the A moieties and the bonds in between leading to the very same specific degrees of polymerization, see equation (88). This number fraction distribution is of most probable type and given by

\[ n_{N,A} = (1 - t)^{N-1}t. \]  

(56)
The number fraction distribution of the bond sequence between A moieties where all $N$ of these inner bonds are of type C is therefore

$$n_{N,C} = \sum_{N=1}^{\infty} n_{N,A} (1 - p_i)^N$$

$$= \frac{t}{1-t} \sum_{N=1}^{\infty} [(1-t)(1-p_i)]^N = \frac{t}{1-t} \sum_{N=1}^{\infty} \left[\frac{(1-r)^2}{s}\right]^N$$

$$= \frac{(1-r)^3(s+r-1)}{(rs+(1-r)^2)(s-(1-r)^2)}.$$

The remaining portion of $1 - n_{NC}$ of all A containing chains is the fraction where all D moieties are located. Since the ratio between inner D and C moieties is $p_j$, we arrive at

$$z_D = \frac{z_A p_j}{1-n_{NC}} = 1 + \frac{rs}{(r+s-1)(1-r)}.$$

Obviously, the number average molar mass, $M_n$, is given by equation (21), since for $M_n$ only the divergence at $r+s = 1$ defines the two different regimes. The above results are compared with simulation data in Figure 8 for the special case of $s = 1/2$. The good agreement between both shows that correlations in the sequence of bonds can be ignored.

For the discussion in the following sections, we also require the number fraction of stable chains, $n_{N,D}$, which is given by

$$n_{N,D} = \sum_{N=1}^{\infty} n_{N,A} p_i^N =$$

$$= \frac{t}{1-t} \sum_{N=1}^{\infty} r^N = \frac{tr}{(1-t)(1-r)}.$$

Similar to the discussion of the preceding sections, we assume most probable weight distributions for $z_A$, $z_C$, and $z_D$, which yields

$$z_{w,A} = z_A (1 + b) = \frac{s+1-r}{(1-r)(s+r-1)},$$

$$z_{w,C} = z_C (1 + b) = \frac{s+1-r}{s+r-1},$$

$$z_{w,D} = z_D (1 + b) = \frac{1-r}{s} + \frac{2r}{s+r-1} + \frac{1}{1-r}.$$
Figure 8. Comparison of simulation data of the case $s = 1/2$ with theory (lines) for average degree of polymerization in case of $1/2 < r < 1$.

As above, computation $M_w$ and $z_w$ requires to consider the weight distribution of the combined chains, here made of A, C, and D moieties. As we shall see below, there is typically $z \gg 1$, which allows to estimate $M_w$ in a simplified manner through

$$M_w \approx z_w \bar{M}$$

(63)

since any correlation that might be important for small $z$ affects only a small weight fraction of all chains. Therefore, we discuss here only the derivation of $z_w$.

There are $2N + 1$ moieties per chain that contains $N$ moieties of type A. The weight fraction of moieties on chains with $N$ moieties of type A among all A containing chains, $w_{N,A}$ is derived using the number fraction distribution of A $N$-mers, $n_{N,A}$, and the corresponding average number of moieties $2z_A + 1$ on these chains:

$$w_{N,A} = \frac{2N + 1}{2z_A + 1} n_{N,A}$$

(64)
\[
\frac{2N+1}{2+t} (1-t)^{N-1} t^2.
\]
The weight average number of moieties on all A containing chains is then
\[
z_{w,A^*} = \sum_{N=1}^{\infty} w_{N,A} \left(2N+1\right)
\]
\[
= \frac{t^2}{2+t} \sum_{N=1}^{\infty} (2N+1)^2 (1-t)^{N-1}
\]
\[
= \frac{t^2 + 8}{(2+t)t}.
\]

In order to obtain \(z_w\) of the full sample, we have to add to \(z_{w,A^*}\) the contribution of the weight fraction \(w_1\) of non-reacted C moieties among all moieties within the sample. A weight fraction of \((1-b)^2\) of all C moieties are non-reacted C moieties, while a number fraction of \(s / (1+s+r)\) is the portion of C moieties among all moieties. Thus, the weight fraction of non-reacted C moieties, \(w_1\), among all moieties (putting \(M_A = M_C = M_D = 1\)) is
\[
w_1 = \frac{s(1-b)^2}{1+s+r} = \frac{(r+s-1)^2}{s(r+s+1)}
\]
thus,
\[
z_w = (1-w_1)z_{w,A^*} + w_1 = \frac{4}{r+s-1} + \frac{2(3r+1)}{(1-r)(1+r+s)}.
\]
This leads to a polydispersity of
\[
\frac{z_w}{z} = \frac{(r-1)s^2 + 2(r-3)(r+1)s + (r-1)^3}{(r-1)(r+s+1)},
\]
which diverges in the limit of \(r \rightarrow 1\) for reasons as discussed for the case of \(r > 1\). The simulation data for the polydispersity of the special case \(s = 1/2\) are compared with the corresponding theoretical expressions in Figure 9.

V. DISCUSSION

A. Dependence on Reaction Rates

In this section, we discuss briefly the impact of reaction rates on average degrees of polymerization. For this purpose, we ran simulations where always one of the reaction rates of the reaction
scheme shown in Figure 1 was either increased or decreased by one order of magnitude in order to test the sensitivity of the molecular weight distributions on reaction rates. As pointed out in the preceding sections, higher order averages like $z_w$ are more sensitive to deviations from the equireactive case. However, our simulation data for $z_w$ shown in Figure 10 indicate only a weak dependence on reaction rates that is visible in the plot only for the two regimes at $r < 1$. We have to point out, that most of the impact of reaction rates stems for the system of Ref. [5] from the asymmetry of A moieties and is absent for symmetric moieties that are all unconnected at the onset of the reactions. In consequence of these observations, we decided not to discuss full analytical solutions for asymmetric A moieties and omit also an explicit discussion based upon reaction rates.
A particularly interesting point of the reactions discussed in the preceding sections is that the bonds with C moieties behave similar to reversible bonds (are able to undergo exchange reactions). Thus, later addition or extraction of C moieties can be used to couple or uncouple stable chain section that are made entirely of A and D moieties, since bonds between the latter are stable. The distribution of these stable sections is the distribution used to compute $n_{N,D}$ and can be found in each section, see equation (22), (40), and (59). However, one has to be aware that there are limitations given by the boundaries between the regimes. Thus, the maximum amount of C moieties that can be taken out in the C-dominated regime is limited by the condition $r + s > 1$ (for homogeneous systems). Also, addition of C moieties can drive the system from the A-dominated regime at $r + s < 1$ into the C dominated regime with $r + s > 1$, however, the way back is impossible as
the total number of bonds to C moieties cannot be reduced.

Also, the stable parts can be modified by either adding some more A or D moieties. If minority species are added such these remain minority, it is sufficient to compute the new ratios \( r \) and \( s \) after the modifications and to use these in the corresponding section. If majority species are added, this can be treated along the D terminated case, since the addition leads to additional non-reacted moieties of the majority species. If the addition drives the system across one of the critical points, the resulting molecular weight distributions will depend on the particular way how the species are mixed and no simple predictions are possible.

Finally, we have to remark that the reversible nature of the exchange reactions can be ceased and the weight distribution can be fixed by terminating all unsaturated C groups by the addition of, for instance, mono-functional A moieties.

C. Optimum Conditions For Minimum Impact of Composition Fluctuations

Another possibility to utilize this particular competing co-polycondensation scheme is to run experiments at the minimum of a particular \( z_X \) or \( z_w \) in the regime with \( r < 1 < r + s \), since there, the specific degrees of polymerization for \( X = A, D \) are rather insensitive towards fluctuations of \( r \) around an average composition, see Figure [9]. Note that we focus here on the irreversible part of the reactions as composition fluctuations of the reversible part can be removed by continuous mixing. The minima are located in the regime \( r < 1 < r + s \) and found for constant \( s > 0 \) through the condition \( \frac{\partial z_X}{\partial r} = 0 \) with \( X = A, D \).

For \( z_A \) (see equation (52)), we obtain for the minimum that

\[
s = 2 - 2r. \tag{69}
\]

Inserting this \( s \) into the expression for \( z_A \), equation (52), leads to

\[
z_A = \frac{2}{1 - r}. \tag{70}
\]

Thus, if a desired \( z_A \) with low polydispersity should be obtained, one solves equation (70) for \( r \), which provides the optimum conditions for synthesis:

\[
\text{r}_{\text{opt},A} = 1 - \frac{2}{z_A} \tag{71}
\]

\[
\text{s}_{\text{opt},A} = \frac{4}{z_A}. \tag{72}
\]
In similar manner, one finds the optimum conditions for polymerizing D moieties to a desired \( z_D \) that

\[
\begin{align*}
  r_{\text{opt},D} &= 1 - \frac{2}{z_D} \\
  s_{\text{opt},D} &= \frac{4}{z_D} \left( 1 - \frac{1}{z_D} \right).
\end{align*}
\]

The sample average degree of polymerization, \( z \), has no minimum for \( r < 1 < r + s \) that could be used to suppress the effect of composition fluctuations on polydispersity. Thus, if only \( z \) needs to be obtained at minimum polydispersity, one simply replaces all irreversible bonds by reversible ones such that all composition fluctuations can decay with time. Finally, \( z_C \) has a trivial minimum at \( s \to \infty \) for polydispersity that cannot be used to tune \( z_C \).

Recent work showed that polydispersity may be reduced for polycondensations that are carried out in small droplets [29]. However, we have to remark that such a strategy is not viable for alternating polycondensations as the relaxation of composition fluctuations is hindered by the boundaries of these small volumes, which enhances the polydispersity.

VI. SUMMARY

In the present paper we have discussed in detail a co-polycondensation, where one “dominating” reacting unit D replaces bonds of the “non-dominant” competitor C with the alternating partner A. This model case is representative for irreversible reactions that compete with exchange reactions for reactions with the same alternating partner. This process leads to three distinct regimes that are characterized by the reaction partner that terminates the polymeric species resulting from the reactions.

For A terminated chains, the competition between D and C is unimportant as the sum of both is in the minority. Therefore, the reaction as a whole is qualitatively equivalent to an alternating co-polycondensation while the specific degrees of polymerization considering only C or D units are obtained by splitting the A terminated chains into populations that contain at least one C or D unit respectively. All averages (number, weight, and specific ones) diverge at the point where the concentrations of both competitors equal the concentration of the alternating partner, 

\[ [C] + [D] = [A]. \]

For D terminated chains, reactions of C units are completely replaced by reactions with D units such that all C units have no bonds. Here, the chains are made of A and D units only whereby
these react according to a perfectly alternating polycondensation. Therefore, the corresponding specific degrees of polymerization of A and D units diverge at $[D] = [A]$, which holds also for the corresponding weight averages. On the contrary, the large number of C units enforces a finite number average molar mass.

For the C terminated regime, the C units are partially replaced by D units inside the chains, such that the specific degree of polymerization of C units diverges at the boundary to the A terminated regime, while it becomes unity at the boundary to the D terminated regime. The specific degrees of polymerization of D and A units diverge both at both boundaries and show a distinct minimum in between, that provides optimum conditions where the reactions are least sensitive towards composition fluctuations. For a desired specific degree of polymerization, one can adjust the stoichiometric ratios such that reactions occur at this least sensitive point. This can be used to reduce the polydispersity of the resulting polymers or to design new co-polycondensation strategies where high molar mass products have been unavailable previously because of incomplete mixing. All weight averages except of C units diverge at both boundaries to the A and D dominated regimes, while the number average molar mass diverges only at the boundary to the A terminated regime.

Exact theoretical expressions for all number and weight average degrees of polymerizations and most molar masses were provided for homogeneous model reactions in the equireactive case (all reaction rates are identical) and at the absence of cyclization. These analytical results were double checked by Monte-Carlo simulations that model the reaction scheme. Furthermore, the kinetic equations describing all reactions were integrated numerically to compare with the simulation data. In all cases, perfect agreement between simulations and kinetic equations was obtained.

Beyond the general discussion of such reactions, we also compared with the specific situation of Ref. [5], where the initial conditions and the asymmetry of the A units introduce a non-random bond sequence and a shift in the specific degree of polymerization of the C units. These resulting correlations become less important the more additional reactions occur as introduced here by D units, such that these can be ignored once there were sufficient D units added to arrive at $[C] + [D] > [A]$. While non-random sequences and reaction rates are important for weight averages and the specific degree of polymerization of the competing units, these correlations have no impact on the average molar mass and the specific degree of polymerization of the alternating partner.
VII. APPENDIX: IDEAL ALTERNATING POLYCONDENSATION

The general mean field solution for alternating polycondensation of molecules of arbitrary functionality was given first by Stockmayer [27] in 1952. Using Flory’s simplifying assumptions of no cyclization and equal reactivity of all reactive groups, the number average, $N_n$, and the weight average degrees of polymerization, $N_w$, as well as $M_n$ and $M_w$ were computed exactly. At full conversion of the minority species, which is typically reached given enough time for reactions and a stoichiometry different from one, $r \neq 1$, the classical result for the degree of polymerization reduces to a simple expression that is solely a function of $r$ for two functional units. The original results were provided in Ref. [27] without derivation. We provide below a quick derivation for the ideal case of a strictly alternating linear polycondensation.

Consider a linear polymerization of two di-functional monomers $X$ and $Y$ that undergo only reactions between $X$ and $Y$ groups without side reactions. Let $r$ denote the ratio of the concentrations $[X]$ and $[Y]$ of reactive groups on $X$ molecules and $Y$ molecules, respectively,

$$r = \frac{[X]}{[Y]}.$$  \hspace{1cm} (75)

For $r \neq 1$, we assume that the reaction terminates when all reactive groups of the minority species are consumed. Therefore, for strictly bimolecular recombination without side reactions, the ratio $r$ connects also the conversions $p_X$ and $p_Y$ of $X$ and $Y$ groups at complete reactions:

$$r = \frac{p_Y}{p_X}. \hspace{1cm} (76)$$

Due to the symmetry of the problem, it is sufficient to discuss only the case of $r < 1$. The end of the reactions is characterized by the minority conversion of here $p_X = 1$, which yields

$$r = p_Y. \hspace{1cm} (77)$$

The non-reacted groups of the majority $Y$ species terminate the chains. If there is no cyclization, all chains will be linear, will have an odd degree of polymerization because of the alternating sequence of $X$ and $Y$, and all chain ends must be of majority type $Y$. The number fraction of $1 - p_Y$ of non-reacted groups (“chain ends”) among all majority $Y$ groups is used to compute the average number of

$$N_Y = \frac{1}{1 - p_Y} = \frac{1}{1 - r}.$$  \hspace{1cm} (78)
majority monomers of type $Y$ per molecule. Since there is always one more majority monomer than minority monomer per linear chain, we obtain for the minority species

$$N_X = N_Y - 1 = \frac{r}{1-r} \quad (79)$$

$X$ monomers per chain. The average number of monomers per chain of both types $A$ and $B$ defines the number average degree of polymerization of the linear chains,

$$N_n = N_X + N_Y = \frac{1+r}{1-r} \quad (80)$$

The reaction is of poly-condensation type, with a most probable number fraction distribution $n_{NY}$ that is controlled by the number $N_Y$ of majority monomers $Y$ per chain. The minority monomers $X$ act effectively as bonds between $Y$ monomers. Thus, the stoichiometric ratio is equivalent to the portion of existing bonds for $r < 1$, see equation (77). This allows to rewrite the expression for the number fractions of chains of a most probable distribution (see equation 1.52 or Ref. [2]) by using $N_Y$ as the degree of polymerization and $r$ as the conversion:

$$n_{NY}(r) = (1-r)r^{N_Y-1}. \quad (81)$$

The weight average degree of polymerization of the linear chains, $N_w$, is computed in the standard way by considering the first and second moment, $m_1$ and $m_2$, of this distribution:

$$N_w = \frac{m_2}{m_1} \quad (82)$$

The first moment is

$$m_1 = \sum_{N_Y=1}^{\infty} n_{NY}(r)(2N_Y - 1) = \frac{1+r}{1-r} = N_n, \quad (83)$$

where $2N_Y - 1$ is the degree of polymerization of a chain counting both $X$ and $Y$ monomers. Similarly, one obtains for the second moment

$$m_2 = \sum_{N_B=1}^{\infty} n_{NB}(r)(2N_B - 1)^2 = \frac{1+6r+r^2}{(1-r)^2}. \quad (84)$$

Thus,

$$N_w = \frac{1+6r+r^2}{1-r^2} \quad (85)$$

These results agree with other mean field derivations, see for instance Refs. [27, 28]. The polydispersity of this reaction is

$$\frac{N_w}{N_n} = \frac{1+6r+r^2}{(1+r)^2} = 1 + \frac{4r}{(1+r)^2}. \quad (86)$$
As mentioned in the introduction, we note that both $N_n$ and $N_w$ diverge for $r = 1$, while the polydispersity remains finite and converges to 2 for $r \to 1$ similar to the classical case of a polycondensation of the same monomers, but with a different function.

For the above ideal alternating polycondensation, each molecules contains at least one $Y$ moiety. Thus,

$$z_Y = N_Y.$$  \hfill (87)

The corresponding result for the minority species is computed by re-normalizing $N_X$ to the portion of molecules that contain $X$ monomers, which is here the portion of chains that are no $Y$ monomers,

$$z_X = \frac{N_X}{1-n_{N_Y=1}(r)} = \frac{N_X}{1-(1-r)} = \frac{1}{1-r} = z_Y.$$  \hfill (88)

Thus, both majority and minority species share the same specific degree of polymerization. These specific weight averages are characterized by the same number fraction distribution, equation (81), which is of most probable type. Let $z_{w,X}$ denote the weight average of the specific degree of polymerization of species $X$. For a most probable distribution, see equation (81), it is known that polydispersity scales as [2]

$$\frac{z_{w,X}}{z_X} = 1 + r,$$

since $r$ refers here to the fraction of existing bonds, i.e. the conversion. Therefore,

$$z_{w,X} = (1 + r) \frac{z_X}{1-r} = z_{w,Y} = N_n.$$  \hfill (90)

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**CONFLICT OF INTEREST**

The authors declare no conflicts of interest.

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Two reactive units compete for the linear co-polycondensation with an alternating third unit such that bonds of the irreversibly reacting unit replace bonds which undergo exchange reactions. Two peaks for the degree of polymerization are observed for the dominating irreversibly reacting and alternating unit as a function of composition. The first peak and the plateau between the peaks can be tuned by adjusting the concentration of units that undergo exchange reactions.

Two reactive units compete for the linear co-polycondensation with an alternating third unit such that irreversible bonds replace bonds which undergo exchange reactions. Two peaks for the degree of polymerization are observed for the dominating and alternating unit as a function of composition. The first peak and the range between the peaks can be tuned by adjusting the concentration of the units that undergo exchange reactions.