

## Bisdithiooxalate as novel coupling agent for amino-terminated polyamides

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## Model reactions

Apart from model reactions of coupling agent **1** with 1-propylamine, model reactions were performed with 1-propanol and 1-butanol under reflux.  $^1\text{H}$  NMR spectra of the reaction mixtures show that these reactions do not yield complete conversion of **1** (see Figure S1). A detailed analysis of the complex reaction mixture was omitted.

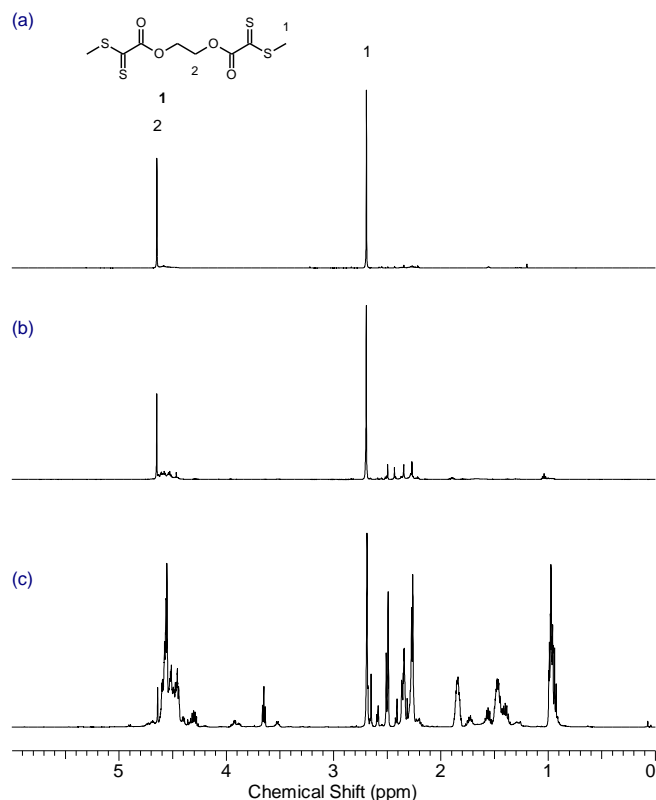


Figure S1:  $^1\text{H}$  NMR spectra of a) ethane-1,2-diyl bis(2-(methylthio)-2-thioacetate) (**1**), b) of **1** after 1h reflux in 1-propanol and c) of **1** after 1h reflux in 1-butanol (solvent:  $\text{CDCl}_3$ ).

## Kinetic approach

Based on the reaction Scheme 2 shown in the main paper, a kinetic model is set up. For this three assumptions are made. First, all ester bonds appearing in the reaction mixture ( $\sim\text{CO-O}\sim$ ,  $\sim\text{CS-SCH}_3$ ,  $\sim\text{CS-O}\sim$ ) are able to react with amino groups resulting in stable amide linking groups ( $\sim\text{CO-NH}\sim$ ,  $\sim\text{CS-NH}\sim$ ). Second, hydroxy groups formed during the reaction undergo exchange reactions with ester groups. Third, the reactivity of all reactive groups does not change during the conversion. In total, seven partial reactions have to be taken into account in a kinetic model describing the coupling reaction (see Scheme 2 of the main paper). For the reacting species, the following designations are used in the model:  $DD$  and  $AB\text{-}CC\text{-}BA$  ( $P$ ) stand for  $\text{NH}_2\text{-PA12-NH}_2$  and **1** respectively,  $\sim A$  ( $\sim\text{CS-SCH}_3$ ),  $\sim C$  ( $\sim\text{OH}$ ), and  $\sim D$  ( $\sim\text{NH}_2$ ) are free reactive groups situated either at the chain ends or as parts of **1**, whereas  $\sim A\text{-}C\sim$  ( $\sim\text{CS-O}\sim$ ) and  $\sim B\text{-}C\sim$  ( $\sim\text{CO-O}\sim$ ) are reactive linking groups. The nonreactive linking groups  $\sim A\text{-}D\sim$  ( $\sim\text{CS-NH}\sim$ ) and  $\sim B\text{-}D\sim$  ( $\sim\text{CO-NH}\sim$ ) are not computed explicitly in the model, as these do not participate in further reactions. But their concentrations are available via the conservation laws given below.  $CC$  (ethylene glycol) is a byproduct which in principle can release the system by

evaporation under reaction conditions. The structure of the polymer chain is described by the sequence of the different chain segments  $\sim AB\text{-}$  ( $\sim\text{CS-CO}\sim$ ),  $\sim CC\text{-}$  ( $\sim\text{O-CH}_2\text{-CH}_2\text{-O}\sim$ ), and  $\sim DD\text{-}$  ( $\sim\text{NH-PA12-NH}\sim$ ) and the respective end groups  $AB\text{-}$  ( $\text{CH}_3\text{-S-CS-CO}\sim$ ),  $CC\text{-}$  ( $\text{HO-CH}_2\text{-CH}_2\text{-O}\sim$ ) and  $DD\text{-}$  ( $\text{NH}_2\text{-PA12}\sim$ ).

The model comprises the primary reactions of the amino groups  $\sim D$  with the dithioester  $\sim A$  (i) and the ester groups  $\sim B\text{-}C\sim$  (ii) of the coupling agent ( $P$ ). In two subsequent reactions the released hydroxy group  $\sim C$  reacts with  $\sim A$  and the resulting thioester group  $\sim A\text{-}C\sim$  reacts with  $\sim D$  according to formulas (iii) and (iv) respectively. Furthermore,  $\sim C$  reacts with  $\sim B\text{-}C\sim$  (v) and  $\sim A\text{-}C\sim$  (vi). These two reactions do not change the fraction of bonds between different reactive groups, but produce free  $CC$  (ethylene glycol) via reaction (vii) (see Scheme 2 of the main paper). Reactions (v)-(vii) reconnect randomly the chain sequences similar to "equilibrium" or "living" polymers<sup>1-3</sup> with the small difference that breakage and reconnection occurs simultaneously.

Polycondensations lead to the formation of a certain amount of cyclic molecules that perturb the computation of molar masses.<sup>4</sup> For simplification, the formation of cyclic molecules is ignored in the following. Then, conversion and number average degree of polymerization are not modified upon reconnecting, which allows to ignore reactions (v)-(vii) for computing average molar masses in a first approximation. Concerning the reactive groups the following reduced set of differential equations is formulated:<sup>5</sup>

$$\frac{d[A]}{dt} = -k_a[A][D] - k_c[A][C] \quad (1)$$

$$\frac{d[B-C]}{dt} = -k_b[B-C][D] \quad (2)$$

$$\frac{d[C]}{dt} = k_b[B-C][D] + k_d[A-C][D] - k_c[A][C] \quad (3)$$

$$\frac{d[A-C]}{dt} = k_c[A][C] - k_d[A-C][D] \quad (4)$$

$$\frac{d[D]}{dt} = -k_a[A][D] - k_b[B-C][D] - k_d[A-C][D] \quad (5)$$

$$\frac{d[P]}{dt} = -2k_a[A][D] - 2k_b[B-C][D] \quad (6)$$

Here, the reaction rates  $k_x$  are used to describe for  $x = a, b, c, d$  the four different types of reactions according to chemical equations (i), (ii), (iii), and (iv) (see Scheme 2 of the main paper). Concerning the initial concentrations of reactive groups it is known that

$$[A]_{t=0} = [B-C]_{t=0} = 2[P]_{t=0}. \quad (7)$$

The mixing ratio

$$r = \frac{[D]_{t=0}}{[A]_{t=0} + [B-C]_{t=0}} = \frac{[D]_{t=0}}{4[P]_{t=0}} \quad (8)$$

connects the initial concentration of  $\sim D$  groups with the possible reaction partners  $\sim A$  and  $\sim B\text{-}C\sim$  of molecules  $P$ . Here,  $r = 1$  refers to a stoichiometric ratio of 1:1 where all  $\sim A$  and  $\sim B\text{-}C\sim$  groups can react with  $\sim D$  and vice versa. Since free  $\sim C$

<sup>5</sup>In the mathematical equations, the indicated bonds ( $\sim$ ) are omitted for simplification. As an example,  $A$  stands for  $\sim A$  and  $B-C$  for  $\sim B\text{-}C\sim$ .

groups compete with free  $\sim D$  groups for binding to  $\sim A$  and  $\sim B-C\sim$ , every second moiety along an infinitely long chain is an  $-AB-$  moiety, while every other moiety must be either of type  $-CC-$  or  $-DD-$  depending on mixing ratio, conversion and reaction rates. The numerical integration of the differential equations allows plotting the concentration changes of all the species involved in the reaction. Examples for  $k_a : k_b : k_c : k_d = 1 : 1 : 1 : 1$  and  $r = 1, 0.75, 0.5, 0.25$  are shown in Figure S2. From the values obtained at quantitative conversion of  $\sim D$ , the theoretically achievable number average molar mass ( $M_n$ ) and a specific degree of polymerization of  $-DD-$  moieties ( $Z_{DD}$ ) can be calculated (see Table S1). Note that this specific degree of polymerization is computed only for those molecules that contain at least one  $-DD-$  moiety in contrast to  $M_n$ , which refers to an average over the whole system including  $CC$ . The numerical integration of the differential equations and Monte-Carlo simulations show that  $M_n$  at full conversion is independent of the reaction rates, whereas  $Z_{DD}$  varies slightly. This observation is corroborated by a detailed mathematical discussion and explicit simulation of the resulting weight distributions.<sup>5</sup> The key results of these studies concerning our particular chemistry are summarized below.

Note that there are three different moieties ( $-AB-$ ,  $-CC-$ , and  $-DD-$ ) that could be used to define a specific “degree of polymerization” by counting these moieties as basic repeating unit. We denote the total average number of moieties per molecule by  $z$  and denote with an index ( $z_{AB}$ ,  $z_{CC}$ , and  $z_{DD}$ ) if specific segments are considered only. These specific averages are of interest if one moiety dominates the molar mass<sup>6</sup> – as in our case  $-DD-$  – or if the chains containing a specific moiety can be separated from the rest or some moieties may evaporate during reactions like ethylene glycol ( $CC$ ).

The total concentration  $2[P]_{t=0}$  of  $A$ ,  $B$ , and  $C$  in any form is not changed during the reactions but interchanges between unbound states  $\sim A$  and  $\sim C$  and bound states  $\sim A-C\sim$ ,  $\sim A-D\sim$ ,  $\sim B-C\sim$ , and  $\sim B-D\sim$ . This provides the following conservation laws:

$$[A-C] + [A-D] + [A] = 2[P]_{t=0} \quad (9)$$

$$[B-C] + [B-D] = 2[P]_{t=0} \quad (10)$$

$$[A-C] + [B-C] + [C] = 2[P]_{t=0} \quad (11)$$

These three equations contain six independent variables.  $[P]_{t=0}$  serves effectively as a normalization condition for concentrations. Below it will be shown that the missing three relations to solve this set of equations can be found by considering three different stoichiometric regimes.

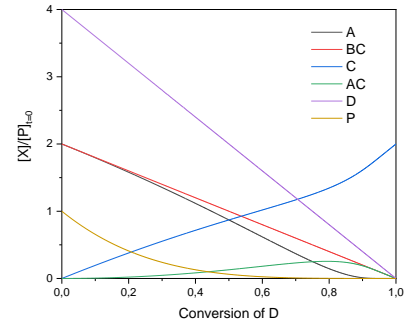
For  $r < 0.5$ , all  $C$  are bound in  $\sim A-C\sim$  and  $\sim B-C\sim$  groups at the end of the reactions resulting in zero unbound  $C$  groups

$$[C] = 0, \quad (12)$$

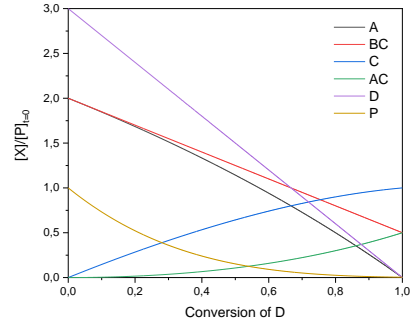
since reactions of  $\sim D$  with  $\sim B-C\sim$  effectively result in the formation of  $\sim B-D\sim$  bonds and subsequently, the released  $\sim C$  groups are converted to  $\sim A-C\sim$  bonds by the reaction with  $\sim A$ . Thus,

$$[A-C] = [B-D]. \quad (13)$$

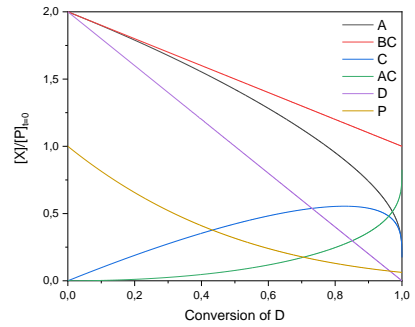
Bound  $A$  exists either as  $\sim A-C\sim$  or  $\sim A-D\sim$ , such that the unbound  $A$  groups amount to



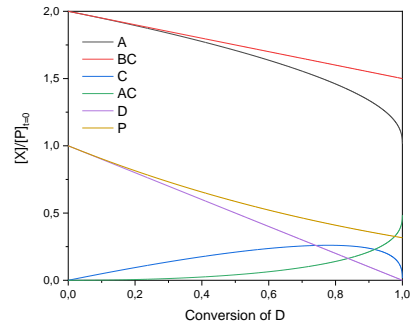
$k_a : k_b : k_c : k_d = 1 : 1 : 1 : 1$  and  $r = 1$



$k_a : k_b : k_c : k_d = 1 : 1 : 1 : 1$  and  $r = 0.75$



$k_a : k_b : k_c : k_d = 1 : 1 : 1 : 1$  and  $r = 0.5$



$k_a : k_b : k_c : k_d = 1 : 1 : 1 : 1$  and  $r = 0.25$

Figure S2: Numerical solutions of the kinetic model for selected parameter sets.

$$[A] = 2(1 - 2r)[P]_{t=0} \quad (14)$$

and

$$[A-D] = 4r[P]_{t=0} - [B-D]. \quad (15)$$

Finally, the ratio in the frequency of connecting chain moieties between  $-AB-$  moieties that are established by  $-DD-$  moieties (containing 2  $D$  groups each) and  $-CC-$  moieties is given by

$$\frac{[D]}{[P]_{t=0}} = 2r. \quad (16)$$

With the above equations and the three conservation laws, all concentrations at the end of the reactions can be computed. Therefore, the final concentrations of reactive groups do not depend on reaction rates. Different reaction rates only control with which probability  $\sim B-C$  and  $\sim B-D$  (or correspondingly  $\sim A-C$  and  $\sim A-D$ ) bonds are formed. This affects the sequence of the moieties, their sequence isomerism, and therefore, can become relevant for the weight average molar mass, but not for the number average molar mass, which is solely determined by the concentration of chain ends.

The probability  $p$  that a given connection between two  $-AB-$  moieties is of type  $-DD-$  is given by

$$p = \frac{2r}{2r+1}. \quad (17)$$

For the regarded case of  $r < 0.5$ , all chains are terminated by excess  $\sim A$  groups at both ends. Let

$$q = \frac{[A]}{2[P]_{t=0}} = 1 - 2r \quad (18)$$

denote the fraction of  $\sim A$  end groups (among all  $A$  groups) that terminate chains. Since each chain has two unreacted ends, the average degree of polymerization as counted by the number  $z_{AB}$  of  $-AB-$  moieties is thus,

$$z_{AB} = \frac{2}{q} = \frac{2}{1-2r}. \quad (19)$$

The number of connecting moieties (either  $-DD-$  or  $-CC-$  sections) is  $z_{AB} - 1$ . Therefore, the average number of moieties per molecule is

$$z = 2z_{AB} - 1 = \frac{3+2r}{1-2r} = \frac{(3+2r)}{(1+2r)} \cdot \frac{(1+2r)}{(1-2r)}. \quad (20)$$

Note that the first factor on the right hand side is the average number of moieties per molecule at the onset of the reaction, while the second factor is equivalent to the classical result for the average degree of polymerization in a linear condensation co-polymerization.<sup>7</sup>

Let  $M_{AB}$ ,  $M_{CC}$ , and  $M_{DD}$  denote the average molar mass of  $-AB-$ ,  $-CC-$  or  $-DD-$  moieties of the chain respectively. The number average molar mass of a molecule at 100 % conversion is then given by

$$\begin{aligned} M_n &= z_{AB}M_{AB} + (z_{AB} - 1)((1-p)M_{CC} + pM_{DD}) \\ &= \frac{1}{1-2r}(2M_{AB} + M_{CC} + 2rM_{DD}). \end{aligned} \quad (21)$$

In our case, the molar mass of the  $-DD-$  moieties is much larger than the mass of the  $-AB-$  or the  $-CC-$  moieties ( $M_{DD} \gg M_{AB}, M_{CC}$ ). Thus, we are interested in the specific degree of polymerization of  $-DD-$  moieties, which is in the equireactive case ( $k_a = k_b = k_c = k_d$ )<sup>5</sup>

$$z_{DD} = \frac{1}{1-2r} - \frac{r}{2} - r^2. \quad (22)$$

Note that this result is not  $\approx M_n/M_{DD}$  in the limit of  $M_{DD} \gg M_{AB}, M_{CC}$  as not all molecules contain  $-DD-$  moieties. Furthermore, the initial condition of  $[B-C]_{t=0} = 2[P]_{t=0}$  introduces a non-random sequence of  $-DD-$  and  $-CC-$  moieties that is propagated through the asymmetry of the  $-AB-$

moieties. This non-randomness is described mathematically by correlation functions (here conditional probabilities), which lead to the second and third term on the right hand side of equation (22). These ‘‘correlations’’ interfere with reaction rates such that  $z_{DD}$  contains a weak additional dependence on reaction rates. This is in contrast to  $M_n$ , and  $z$  that depend only on the stoichiometric ratio  $r$ . For the non-equireactive cases, simple exact solutions are not available. Here, Monte-Carlo simulations provide the missing information.<sup>5</sup>

For  $0.5 < r < 1$ , there are sufficient  $\sim D$  groups to saturate all  $A$  and  $B$  groups by bonds with either  $D$  or  $C$  groups ( $-AD-$ ,  $-BD-$ ,  $-AC-$ ,  $-BC-$ ). Thus, it is clear that

$$[A] = 0. \quad (23)$$

Excess  $\sim D$  groups beyond  $r = 0.5$  cause the formation of unbound  $\sim C$  groups

$$[C] = 4(r - 1/2)[P_0]_{t=0}, \quad (24)$$

which terminate chains at complete reaction. Similar to above, it is computed

$$q = \frac{[C]}{2[P_0]_{t=0}} = 2r - 1 \quad (25)$$

as the fraction of  $\sim C$  terminal groups (among all  $C$  groups). The specific degree of polymerization of  $-CC-$ ,  $-CC$ , and  $CC$  moieties is then

$$z_{CC} = \frac{1}{q} \quad (26)$$

There are  $2r$   $-DD-$  moieties per  $-CC-$  moiety. Thus, there is in average a total of

$$z_{CD} = \frac{2r+1}{q} = \frac{2r+1}{2r-1} \quad (27)$$

$-CC-$  and  $-DD-$  moieties per molecule (including isolated  $CC$  moieties), while the average number of  $-AB-$  moieties is  $z_{CD} - 1$ . Therefore,

$$z = 2z_{CD} - 1 = \frac{3+2r}{2r-1}, \quad (27)$$

which is symmetric (with respect to a change in sign) to equation (20). The same statement holds for the number average molar mass of the reaction mixture, which is given by

$$M_n = \frac{1}{2r-1}(2M_{AB} + M_{CC} + 2rM_{DD}). \quad (28)$$

For  $0.5 < r < 1$ , correlations are ignorable<sup>5</sup> for  $z_{DD}$  and one obtains for the equireactive case

$$z_{DD} = 1 + \frac{r}{(2r-1)(1-r)}. \quad (29)$$

Note that for  $r \rightarrow 1$  there is (theoretically) only one chain containing all  $-AB-$  and  $-DD-$  moieties while the rest of the molecules are isolated  $CC$  moieties. The presence of these moieties in the above equation prevents the observation of a diverging  $z$  in this limit, however, this divergence is visible in the behaviour of  $z_{DD}$  for  $r \rightarrow 1$ .

A quite interesting point of the parameter range  $0.5 < r < 1$  is that isolated  $CC$  moieties (ethylene glycol) formed through reactions (v)-(vii) may be taken out of the system continuously by evaporation. This leads to a redistribution of unbound  $\sim C$  groups that drives a constant increase of the average degree of polymerization, which is finally diverging when no more  $CC$  can be taken out of the reaction mixture. This can be treated using the above relations by considering the total amount of  $CC$  moieties ( $CC$ ,  $-CC$ ,  $-CC-$ ) in the system in relation to  $DD$  moieties ( $-DD$ ,  $-DD-$ ). The maximum fraction of  $CC$  moieties that can be removed from the system is  $q/2$ , which is half of the portion of unbound  $\sim C$  groups. When removing less than these from the system, the remaining unbound groups  $C$  set the degree of polymerization via a renormalized  $q$  as these groups terminate the chains.<sup>5</sup> For the same reasons as given for  $r < 0.5$ ,  $z_{DD}$  values for non-equireactive cases are only available through Monte-Carlo simulations.<sup>5</sup>

At  $r \geq 1$ , it is no longer possible to obtain an infinite degree of polymerization by removing  $CC$ , since  $CC$  is already released quantitatively by the reaction of excess  $\sim D$  groups with  $\sim A-C\sim$  and  $\sim B-C\sim$ . Then, all  $C$  groups are unbound

$$[C] = 2[P_0]_{t=0} \quad (30)$$

and there are no unbound  $A$  and  $B$  groups

$$[A] = [B] = 0 \quad (31)$$

at the end of the reactions. In this case, excess  $\sim D$  groups terminate the growing chains. Similar to above, the fraction of unbound  $\sim D$  groups at the end of the reactions is used to define

$$q = \frac{[D]}{[D]_{t=0}} = \frac{[D]_{t=0} - 4[P_0]_{t=0}}{[D]_{t=0}} = \frac{r-1}{r}. \quad (32)$$

Here, the average degree of polymerization is computed most conveniently in numbers of  $z_{DD}$  moieties ( $-DD-$ ,  $DD-$ ,  $DD$ ) with a number  $z_{DD} - 1$  of  $-AB-$  moieties in between while ignoring isolated  $CC$  moieties. Then, the average degree of polymerization is simply

$$z_{DD} = \frac{1}{q} = \frac{r}{r-1}. \quad (33)$$

The average molar mass (without ethylene glycol) is then computed by

$$M_n = (z_{DD} - 1)M_{AB} + z_{DD}M_{DD}. \quad (34)$$

If one considers all molecules in the reaction mixture including  $CC$  (ethylene glycol), one obtains the same results for  $z$  and  $M_n$  as for the case  $0.5 < r < 1$ . In difference to the two previous cases,  $z_{DD}$  cannot depend on reactivity ratios, since all  $CC$  moieties are expelled from the chains and all  $-AB-$  moieties are completely reacted, which leaves no possibility for a preferred bond type.

In summary, we obtain for all regimes that

$$z = \frac{2r+3}{|2r-1|} \quad (35)$$

and

$$M_n = \frac{1}{|2r-1|} (2M_{AB} + M_{CC} + 2rM_{DD}), \quad (36)$$

while different results are obtained for  $z_{DD}$  in each regime.<sup>5</sup> For  $r < 0.5$ , correlations due to initial conditions are important, while reaction rates provide additional corrections. For the equireactive case one obtains

$$z_{DD} = \frac{1}{1-2r} - \frac{r}{2} - r^2. \quad (37)$$

For  $0.5 < r < 1$ , correlations become ignorable while reaction rates still cause small corrections. The equireactive case provides here

$$z_{DD} = 1 + \frac{r}{(2r-1)(1-r)}. \quad (38)$$

For  $r > 1$ , there is

$$z_{DD} = \frac{1}{q} = \frac{r}{r-1} \quad (39)$$

independent of correlations and reaction rates.

For the equireactive case, the calculated dependencies of the degree of polymerizations  $z$  and  $z_{DD}$  on the mixing ratio  $r$  are shown in Figure S2 as examples. It is worth mentioning that the calculated values and the values obtained by Monte Carlo simulation agree very well. Regarding the assessment of the coupling behavior,  $z$  is not very meaningful due to the large difference in molar mass between the moieties,<sup>6</sup> since the inclusion of  $CC$  limits the information concerning the molar mass increase of the polymer. However, this information is provided by  $z_{DD}$ . Specifically, the  $z_{DD}$  curve shows two maxima at  $r = 0.5$  and  $1$ , which is a consequence of the four reactive centers of the coupling agent. In addition, the  $z_{DD}$  values between the two maxima are relatively high, which in practice suggests good coupling conditions over a wide concentration range of the coupling agent. Non-equireactive cases differ slightly from the equireactive cases, but also show the typical two maxima (see Table S1).

Results for all specific degrees of polymerization including a general derivation of the above results can be found in Ref.<sup>5</sup>

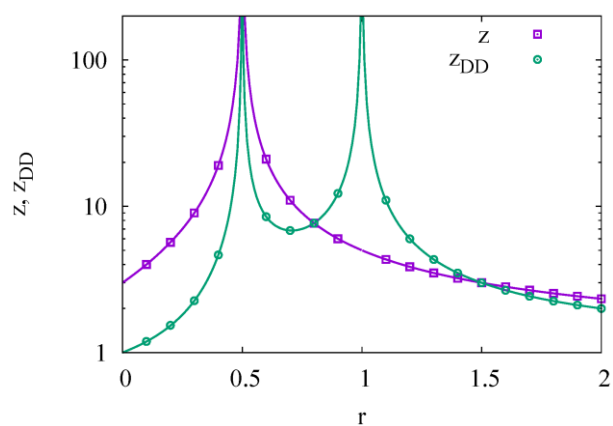


Figure S3: Theoretical degrees of polymerization in dependence on mixing ratio  $r$  for the equireactive conversion of  $AB-CC-BA$  with  $DD$  ( $k_a = k_b = k_c = k_d$ ).  $z$  considers all molecules in the reaction mixture including released  $CC$ .  $z_{DD}$  is the specific degree of polymerization considering all  $DD$  containing molecules. Lines are numerical solutions of the model calculated using equations (35)-(39). Points are based on Monte-Carlo simulations.<sup>5</sup>

Table S1: Numerical solutions of the kinetic model for selected sets of reaction rates  $k_x$  and mixing ratios  $r$  after complete conversion. For all calculations, the starting amount of  $P$  ( $AB-CC-BA$ ) was set to 1.

No.	$k_a : k_b : k_c : k_d$	$r$	[A]	[C]	[D]	[A-C]	[B-C]	[A-D]	[B-D]	$Z_{DD}$
A <sub>1</sub>	1 : 1 : 1 : 1	1.00	0.0	2.0	0.0	0.0	0.0	2.0	2.0	$\infty^1) / \infty^2)$
A <sub>2</sub>	1 : 1 : 1 : 1	0.75	0.0	1.0	0.0	0.5	0.5	1.5	1.5	$7.00^1) / 7.01^2)$
A <sub>3</sub>	1 : 1 : 1 : 1	0.50	0.0	0.0	0.0	1.0	1.0	1.0	1.0	$\infty^1) / \infty^2)$
A <sub>4</sub>	1 : 1 : 1 : 1	0.25	1.0	0.0	0.0	0.5	1.5	0.5	0.5	$1.81^1) / 1.82^2)$
B <sub>1</sub>	10 : 1 : 1 : 1	1.00	0.0	2.0	0.0	0.0	0.0	2.0	2.0	$\infty^2)$
B <sub>2</sub>	10 : 1 : 1 : 1	0.75	0.0	1.0	0.0	0.02	0.98	1.98	1.02	$6.07^2)$
B <sub>3</sub>	10 : 1 : 1 : 1	0.50	0.0	0.0	0.0	0.34	1.66	1.66	0.34	$\infty^2)$
B <sub>4</sub>	10 : 1 : 1 : 1	0.25	1.0	0.0	0.0	0.11	1.89	0.89	0.11	$1.99^2)$
C <sub>1</sub>	1 : 1 : 0.1 : 1	1.00	0.0	2.0	0.0	0.0	0.0	2.0	2.0	$\infty^2)$
C <sub>2</sub>	1 : 1 : 0.1 : 1	0.75	0.0	1.0	0.0	0.5	0.5	1.5	1.5	$7.01^2)$
C <sub>3</sub>	1 : 1 : 0.1 : 1	0.50	0.0	0.0	0.0	1.0	1.0	1.0	1.0	$\infty^2)$
C <sub>4</sub>	1 : 1 : 0.1 : 1	0.25	1.0	0.0	0.0	0.5	1.5	0.5	0.5	$1.81^2)$

1) Numerical solution of the kinetic model

2) Obtained by Monte-Carlo simulation according to ref.<sup>5</sup>

## NMR characterization of the amino-terminated PA12 used in this study

Figure S4 and Figure S5 depict the <sup>1</sup>H and <sup>13</sup>C NMR spectrum, respectively, of PA12-NH<sub>2</sub> ( $M_n = 2100$  g/mol) with assignment of the backbone signals. The amino-terminated PA12 used in this study contains 4,4'-diaminodicyclohexylmethane to regulate the molecular weight. 4,4'-Diaminodicyclohexylmethane is incorporated in the polymer chain both as diamide but also results in secondary amino end groups. However, the dominating end group is the primary amino end group from PA12 (Scheme S1).

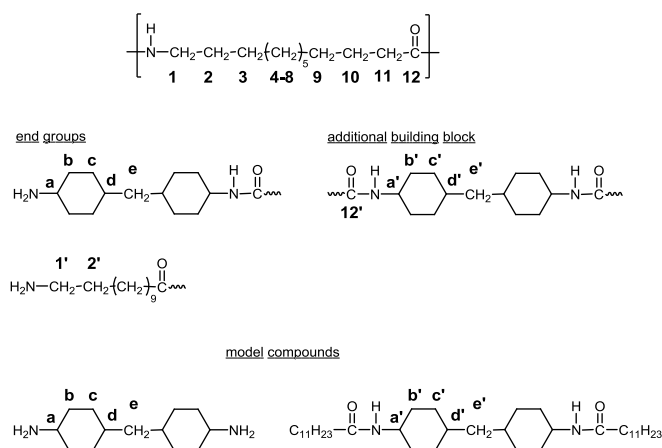
To distinguish these structures from new structures formed in the coupling process, their characteristic signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the amino-terminated PA12 were assigned based on NMR studies on appropriate model compounds: 4,4'-diaminodicyclohexylmethane and 4,4'-dilaurylamidedicyclohexylmethane (Figures S6 – S9). Both compounds as well the reacted 4,4'-diaminodicyclohexylmethane in the polymer exist in three different geometric configurations, trans,trans (tt), cis,trans (ct), and cis,cis (cc). Only two signals appear for the 4,4'-methine group due to cis and trans configuration of the cyclohexyl ring. The major isomer is the trans isomer.

The compounds were measured in CF<sub>3</sub>COOD. Therefore, proton – deuteron exchange results in partial deuteration of the amide groups and in deuteration / protonation of the amino groups.

### Selected <sup>1</sup>H and <sup>13</sup>C signals of the amino-terminated PA12

<sup>1</sup>H NMR (TFA-*d*): 4.19 (a'<sub>c</sub>), 3.93 (a'<sub>t</sub>), 3.60 (a<sub>c</sub>), 3.55 (1), 3.32 (a<sub>t</sub>), 3.22 (1'), 2.71 (11), 1.78 (2'), 1.76 (10), 1.69 (2), 1.5 – 1.2 ppm (3-9).

<sup>13</sup>C NMR (TFA-*d*): 181.3 (12), 180.8 (12'<sub>c</sub>), 180.4 (12'<sub>t</sub>), 55.7 (a'<sub>t</sub>), 54.9 (a<sub>t</sub>), 53.6 (a'<sub>c</sub>), 53.4 (a<sub>c</sub>), 44.9 (1), 43.4 (1'), 35.4 (11), 30.8, 30.7, 30.6 and 30.3 (4-9), 29.3 (2), 28.8 (2'), 28.0 (3), 27.4 ppm (10).



Scheme S1 Structures of polyamide 12 (PA12), amino end groups, the incorporated 4,4'-diaminodicyclohexylmethane unit and the model compounds 4,4'-diaminodicyclohexylmethane and 4,4'-dilaurylamidedicyclohexylmethane. In TFA-*d* solution used for NMR measurements the amino groups are protonated / deuterated.

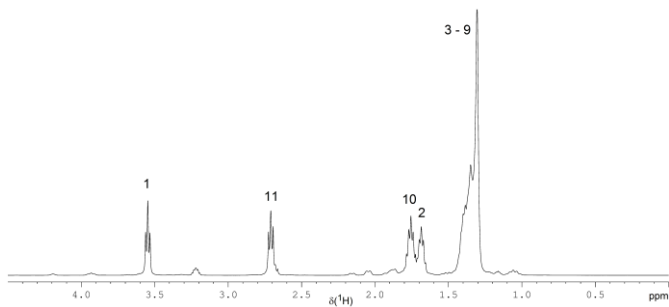


Figure S4:  $^1\text{H}$  NMR spectrum of amino-terminated PA12 (2100 g/mol) in TFA-*d*.

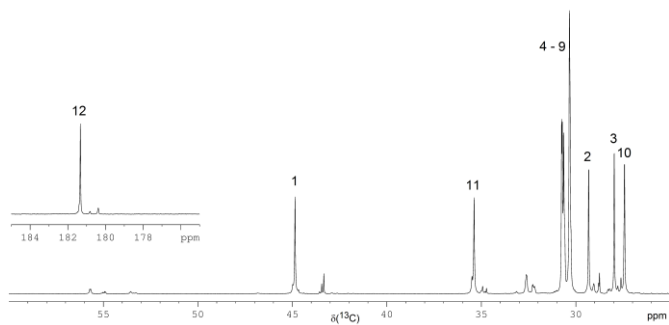


Figure S5:  $^{13}\text{C}$  NMR spectrum of amino-terminated PA12 (2100 g/mol) in TFA-*d*.

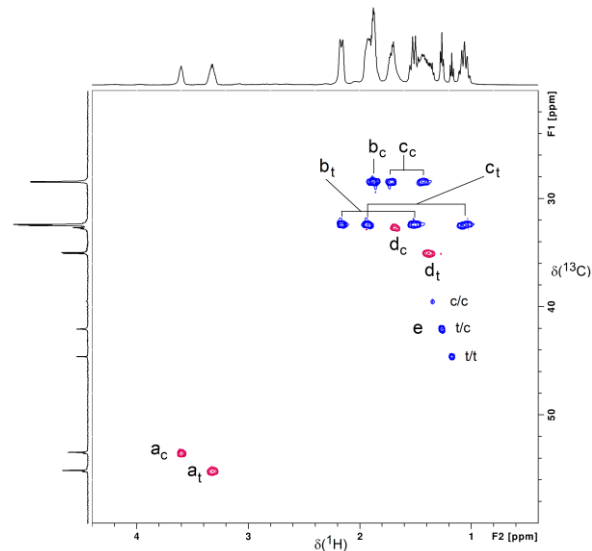


Figure S8: Edited HSQC spectrum (red: CH; blue:  $\text{CH}_2$ ) of 4,4'-diaminodicyclohexylmethane (mixture of isomers) in TFA-*d* showing the assignment of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals. The amino groups are protonated/deuterated.

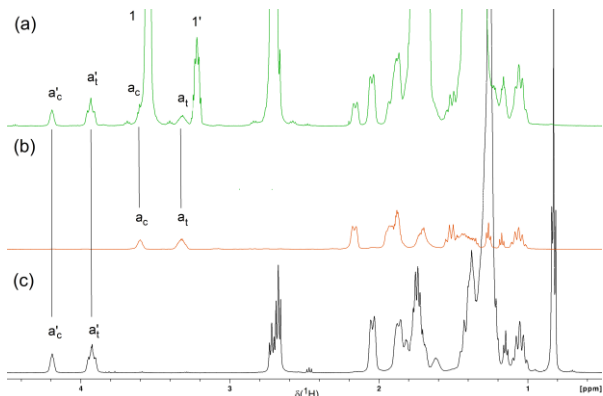


Figure S6:  $^1\text{H}$  NMR spectra of (a) amino-terminated PA12 with assignment of methylene group 1' and methine groups a and a', (b) 4,4'-diaminodicyclohexylmethane (mixture of isomers) and (c) 4,4'-dilaurylamidedicyclohexylmethane (mixture of isomers) in TFA-*d*. The amino groups are protonated/deuterated.

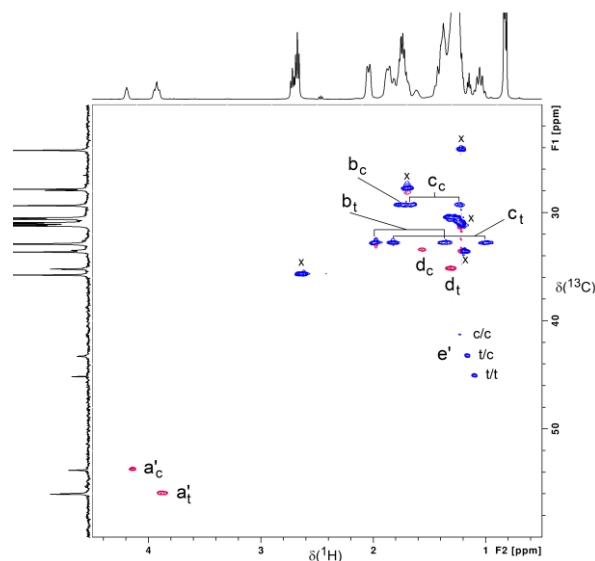


Figure S9: Edited HSQC spectrum (region, red: CH; blue:  $\text{CH}_2$ ) of dilaurylamidedicyclohexylmethane (mixture of isomers) in TFA-*d* showing the assignment of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals. Signals of the lauryl moiety are marked with a cross.

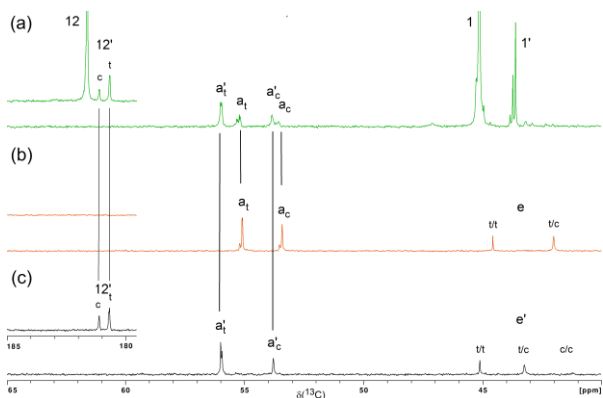


Figure S7:  $^{13}\text{C}$  NMR spectra (regions) of (a) amino-terminated PA12 with assignment of methylene group 1' and methine groups a and a', (b) 4,4'-diaminodicyclohexylmethane (mixture of isomers) and (c) 4,4'-dilaurylamidedicyclohexylmethane (mixture of isomers) in TFA-*d*. The amino groups are protonated/deuterated.

## NMR characterization of PA12 after reaction with coupling agent **1**

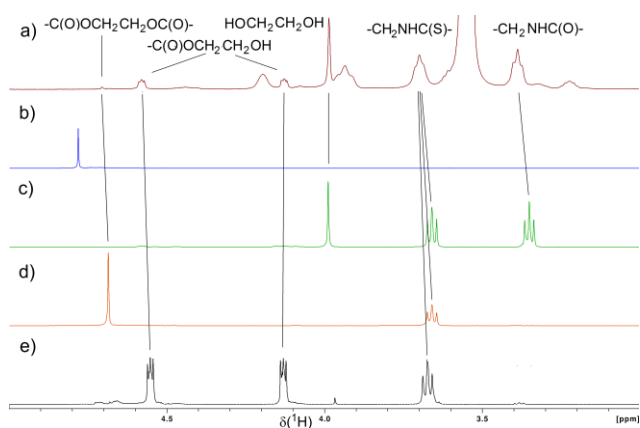


Figure S10:  $^1\text{H}$  NMR spectra (region) of a) PA12-NH<sub>2</sub> (2100 g/mol) melt-reacted with **1** ( $r = 1$ ), b) **1**, c) **4c**, d) **4d** and e) **4e** in TFA-*d* showing the assignment of new  $^1\text{H}$  NMR signals of the reacted PA12.

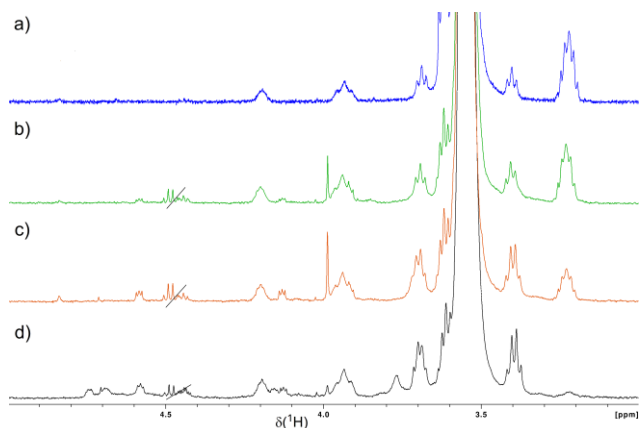


Figure S11:  $^1\text{H}$  NMR spectra (region) of a) PA12-NH<sub>2</sub> (15400 g/mol), b) **M1**, c) **M2** and d) **M3** in TFA-*d*.

## SEC curves of chain extended PA12

Table 2 of the original paper contains molar masses of chain extended PA12 samples. Respective SEC curves are shown in Figure S12

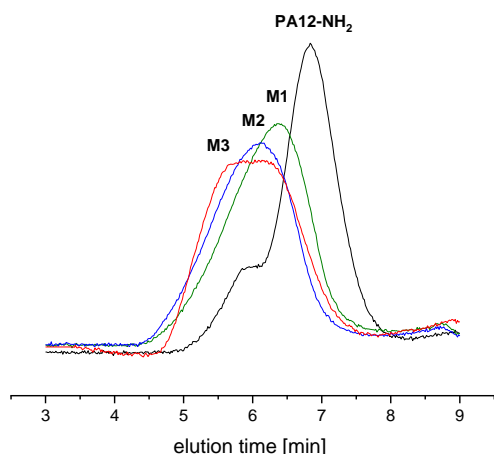


Figure S12: SEC curves of PA12-NH<sub>2</sub> and chain extended samples **M1**, **M2**, and **M3**.

## Notes and References

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