# Supplementary Information for "A unified kinetic Monte Carlo approach to evaluate (a)symmetric block and gradient copolymers with linear and branched chains illustrated for poly(2-oxazoline)s"

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#### S1 Model validation of kinetic parameters

In this section, the adequacy of the kinetic parameters in Table 1 of the main text to describe experimental size exclusion chromatography (SEC) traces is demonstrated. Focus is on the synthesis of 70/30 MeOx/PhOx copolymers with various target degrees of polymerization (target DP's). Firstly, model validation for the the batch production of gradient copolymers is considered. Secondly, the semi-batch production of diblock copolymers is considered.

S1.1. Model validation for the 70/30 gradients at various target DP



Fig. S1 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for CROP of MeOx and PhOx ( $[M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}$ ;  $[M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 150) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 4.70  $\cdot$  10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S2 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for CROP of MeOx and PhOx ( $[M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}$ ;  $[M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 120) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 3.56  $\cdot$  10<sup>-2</sup>, the chain

length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S3 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for CROP of MeOx and PhOx ( $[M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}$ ;  $[M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 100) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 2.80  $\cdot$  10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S4 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for CROP of MeOx and PhOx ( $[M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}$ ;  $[M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 80) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 2.04  $\cdot$  10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S5 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for CROP of MeOx and PhOx ( $[M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}$ ;  $[M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 60) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening  $1.28 \cdot 10^{-2}$ , the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).

S1.2. Model validation for the 70/30 blocks at various target DP



Fig. S6 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for the di-block CROP of MeOx and PhOx ( $[M]_0 = 3$  mol·L<sup>-1</sup>;  $[M_A]_0$ :  $[M_B]_0 = 70:30$ ; target degree of polymerization of 150) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 4.70  $\cdot$  10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S7 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for the di-block CROP of MeOx and PhOx  $([M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}; [M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 120) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening  $3.56 \cdot 10^{-2}$ , the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S8 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for the di-block CROP of MeOx and PhOx ( $[M]_0 = 3$  mol·L<sup>-1</sup>;  $[M_A]_0$ :  $[M_B]_0 = 70:30$ ; target degree of polymerization of 100) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 2.80  $\cdot$  10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S9 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for the di-block CROP of MeOx and PhOx  $([M]_0 = 3 \text{ mol}\cdot\text{L}^{-1}; [M_A]_0: [M_B]_0 = 70:30$ ; target degree of polymerization of 80) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening 2.04 · 10<sup>-2</sup>, the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S10 (a) Comparison between experimental (blue line) and simulated (green line) SEC trace at an overall monomer conversion of 0.97 for the di-block CROP of MeOx and PhOx ( $[M]_0 = 3$ mol·L<sup>-1</sup>;  $[M_A]_0$ :  $[M_B]_0 = 70:30$ ; target degree of polymerization of 60) in acetonitrile at 140 °C; also shown is the deconvolution of the simulated SEC trace in the contribution of the linear (purple line) and branched (red line) species. (b) corresponding cumulative distributions. All simulated distributions have been corrected by considering a Gaussian broadening  $1.28 \cdot 10^{-2}$ , the chain length of branched macrospecies has been additionally multiplied by a factor of 1.1 (difference in hydrodynamic volume; aspect of calibration with linear standards).



Fig. S11 Summary with extra experimental validation (countercase for Figure 2 in the main text for the 70:30 gradient case) (a) Comparison between experimental SEC traces (solid lines) and simulated SEC traces after applying a molar mass shift for the branched species by a factor of 1.1 and SEC-broadening (dotted lines) for the di-block CROP of MeOx (A) and PhOx (B) ( $[M]_0=3$ mol·L<sup>-1</sup>;  $[M_A]_0:[M_B]_0=70:30$ ; target degree of polymerizations (DP) ranging between 30 and 150) in acetonitrile at 140 °C; (b) the cumulative SEC traces corresponding to (a); (c) simulated monomer conversion profiles; (d) and (e), the simulated data (lines) of number average chain length  $x_n$  and dispersity D are compared to experimental data (symbols). Also given in table format the SEC broadening parameters.

# S2. Calculation of average structural deviation of a linear chain/segment: $\langle$ SD> value In what follows, the main mathematical principles are highlighted. These principles are extensions with respect to the earlier work of Van Steenberge *et al.*<sup>1</sup> (finetuned in Fierens *et al.*<sup>2</sup>) and Toloza *et al.* dealing with symmetric gradients and di-blocks.

### Step 1: Ideal reference cases with 1000 chains based on monomer inclusion probabilities profiles (cf. Figure 3 in the main text)

As explained in the main text, the ideal references cases are defined based on 1000 chains and a given fixed chain length. The simulation of an ideal product is thus limited to a finite population size of monomer units that can be subjected to floating point number probabilities, as shown via the monomer inclusion probabilities in the top row of Fig. 3 (A: blue; B: green).

Specifically, for the gradient sections of the polymer products ( $T_1: 1 \le y \le 150$  and  $T_2: 1 \le y \le 60$  with y the chain position from "left" to "right"), the ideal products can only approximate the designed monomer inclusion probability profiles, and, hence, the targeted compositional distribution. In contrast, for the targeted block sections of the ideal products ( $T_2: 61 \le y \le 150$ ) and  $T_3: 1 \le y \le 150$ ), the finite population size does not introduce any imperfections, since the monomer inclusion probability profiles are then integer numbers. This means that for  $T_3$ , which is a complete block, there are only integer values.

This difference between the gradient and block sections is also visible in the cumulative amount of A and B units (*S* value) in a single chain randomly selected from the "ideal product". This is illustrated by plotting  $S_{i,A/B,real\ chain}(y)$  for the three targets (i = 1, 2, 3) in the bottom row of Figure 3 (counting A: blue, counting B: green). Indeed, only the block sections of the targeted compositional distributions show a smooth profile for the total amounts of A and B ( $T_2$ : 61  $\leq$  $y \leq 150, T_3$ :  $1 \leq y \leq 150$ ).

The general ( $x_{A \text{ and }} x_{B}$  relative overall contributions) monomer inclusion probabilities for a chain with length  $\omega$  for  $T_{1}$ ,  $T_{2}$  and  $T_{3}$  are given by:

(for 
$$T_1$$
)  $p_{1,A}(y) = 1 - \frac{2x_B(y-1)}{(\omega-1)}$  (S1)

(for 
$$T_2$$
)  $p_{2,A}(y < (x_A - x_B)\omega) = 1$  (S2)

$$p_{2,A}(y \ge (x_A - x_B)\omega) = \frac{1}{2} - \frac{y - 1 - x_A(\omega - 1)}{2x_B(\omega - 1)}$$
(for T<sub>3</sub>)
$$p_{3,A}(y < x_A\omega) = 1$$

$$p_{3,A}(y \ge x_A\omega) = 0$$
(S3)

Note that A and B can be switched here dependent on the preference of the use, as for instance clear from Equation (*S*3) in which a A-B block is considered but this could be changed in a B-A block (shortly disclaimer 1).

 $S_{i,A/B,ideal}(y)$  can be mathematically expressed as the *y*-dependent cumulative monomer inclusion probability functions for a chain of length  $\omega$ :<sup>1</sup>

$$S_{i,A/B,ideal}(y) = \sum_{y=1}^{\omega} p_{\omega,A/B}(y)$$
(S4)

In general, as explained in Van Steenberge *et al.*<sup>1</sup>, one has thus 4 ideal S profiles, as one can apply Equation (S4) assuming either a A to B or a B to A case, reminding disclaimer 1.

### Step 2: Comparison with a specific copolymer composition from a polymerization recipe (cf. Figure 4(a) and Figure 4(b) in the main text).

The simulated (or simply "actual") cumulative amount of the monomer types A and B in every chain z and for every position  $y(S_{A/B}(y, z))$  can be retrieved from the matrix-based *k*MC simulations.

To quantify the (absolute) structural deviation (SD\*) between the studied copolymer system and the theoretical reference molecule, the actual *S*-functions are compared to the theoretical *S*-functions for every position y in every chain z in the *k*MC ensemble, and this in every direction of the copolymer chains. As explained in earlier work the storing of a chain from "left" to "right" or from "right" to "left" should result in the same structural quality.<sup>1</sup>



Fig. S12 Top: Illustration of a symmetrical (a) and asymmetrical (b) gradient (top) and block (bottom) copolymer. While storing the copolymer composition from "left to right" or from "right to left" give the same quality, interchanging monomers A and B will give different structures when asymmetrical copolymers are considered. Bottom: Normalization constants for T<sub>1</sub> (gradient; purple lines), T<sub>2</sub> (block-gradient; green lines) and T<sub>3</sub> (di block; blue lines) for 50 % (c) and 30 % (d) functionalized A/B-copolymers at different fixed chain lengths (here denoted as target DP).

In this context, for the three targets (i=1,2,3), the  $SD_i ** (y,z)$  parameter evaluates the chains form "left" to "right", *i.e.* from the  $\alpha$ -monomer to the  $\omega$ -monomer, and, the  $SD'_i ** (y,z)$ parameter evaluates the chains from "right" to "left", *i.e.* from the  $\omega$ -monomer to the  $\alpha$ -monomer. Focusing only the former it has been derived in Van Steenberge et al.<sup>1</sup> that following comparison should be considered:

$$SD_{i} ** (y, z) = \sum_{y=1}^{\omega} \frac{1}{2} \frac{|S_{i,A,Ideal}(y) - S_{A}(y, z)| + |S_{i,B,Ideal}(y) - S_{B}(y, z)|}{\omega^{2}}$$
(S5)

As counting of both A and B is done an averaging with a factor 0.5 is done. The first normalization with  $\omega$  is done to express the deviation per monomer units and the second

normalization with  $\omega$  is performed to treat chains with different chain length in the same manner, as inherently a longer chain can have more deviations.

For a given target thus *i*, reminding disclaimer 1, one can thus calculate  $2 SD_i * (y, z)$  and  $2 SD'_i * (y, z)$  profiles. The minimum of the 4 values should be selected for each (y, z) to deliver  $SD^*_i(y, z)$  as used in Figure 1 in the main text.

As highlighted in previous work with symmetric amounts (gradient<sup>1</sup> and block<sup>3</sup>) the consideration of 4 deviations can be relevant, as for those systems, there can be the need of the constraint that upon interchanging the monomer types A and B the structural quality should not change (cf Fig. S12, left). However, more asymmetric comonomer compositions will show less molecular equality between polymers if A and B are interchanged (cf. Fig. S12, Right) so that two structural deviation parameters  $SD_i$  \*\* and  $SD'_i$  \*\* (assuming the A to B build-up) suffice. Hence, it then holds:

$$SD_i^*(y, z) = min\{SD_i^* * (y, z), SD_i^* * (y, z)\}$$
(S6)

Practically one aims at an average value so that all the individual  $SD_i^*$  values are summed up and divided by  $z_{\text{max}}$ , which is the number of copolymer chains stored:<sup>1</sup>

$$\langle SD_i^* \rangle = \sum_{z=1}^{z_{max}} \frac{SD_i^*}{z_{max}}$$
(S7)

#### Step 3: Normalization (cf. y-axis in Figure 4(c))

The  $\langle SD_i^* \rangle$  value can be rescaled dividing by the homopolymer value ( $\langle SD_i^* \rangle_{HP}$ ), which as explained in the main text can be seen as the worst case scenario:<sup>1</sup>

$$\langle SD_i \rangle = \frac{\langle SD_i^* \rangle}{\langle SD_{i,HP}^* \rangle} \tag{S8}$$

which has a value between 0, corresponding to a perfect compositional distribution, and 1, which corresponds to a homopolymer.

In case of a symmetric comonomer composition, the monomer identity (*A* or *B*) of the hypothetical homopolymer used to calculate the normalization constant  $\langle SD_i^* \rangle_{HP,A/B}$  does not affect the value of this normalization constant. On the other hand, for asymmetric comonomer compositions, if the hypothetical homopolymer consists of the monomer present in the system in lower amounts, the deviation to the targeted composition distribution should be greater than compared to a homopolymer consisting of the predominant monomer. Hence, in general two  $\langle SD_i^* \rangle_{HP}$  values should be calculated, namely  $\langle SD_i^* \rangle_{HP,A}$  and  $\langle SD_i^* \rangle_{HP,B}$  and then a maximal  $\langle SD_i^* \rangle_{HP}$  should be selected:

$$\langle SD_{i,HP}^* \rangle = max\{\langle SD_{i,HP,A} \rangle, \langle SD_{i,HP,B} \rangle\}$$
(S8)

In Fig. S12 (bottom), the calculated normalization constants  $\langle SD_i^* \rangle_{HP}$  are shown for two B-functionalization % values. The above described concept is reflected in the decreasing trend for  $\langle SD_i^* \rangle_{HP}$  if the symmetry of the comonomer composition increases.

Step 4: Introduction of threshold values (e.g.  $\langle SD_i \rangle_{Good}$  lines in Figure 4(c) and Figure 10 in the main text) Two threshold  $\langle SD_i \rangle$  parameters ( $\langle SD_i \rangle_{Exc}$  and  $\langle SD_i \rangle_{Good}$ ) has been defined for each  $T_i$  to introduce a quality classification system, which consists of three quality classes: excellent, good and poor. It should be stressed that these thresholds are somewhat arbitrary but as explained in the main text there is a reasoning behind the currently selected values. With more and more simulation data available it becomes also more evident to safely select reasonable threshold values.

Figure S13 gives on overview of a couple of evaluations to highlight why it makes sense to have a lower  $\langle SD_i \rangle_{Good}$  for asymmetric contribution, namely of value of 0.13 vs. 0.3, the previous value for symmetric contributions. The 0.05  $\langle SD_i \rangle_{Exc}$  is only a bit higher than the values of the ideal references case so that it makes sense to have such value to really identify very well structured chains. Also here examples are included in Figure S13 to make this more clear.



Fig. S13 Examples of evaluations to explain the currently selected threshold values.

The top part of Figure S13 relates to symmetric contributions. Structure II in the first row is not perfect in structure compared to the targeted di-block but its construction with only a 20% deviation is must be seen as a reasonable structure vs the selected target. The  $\langle BD \rangle$  is 0.06, which is close to the 0.05 threshold. If one considers a full gradient (but with fixed chain lengths; Structure III) a  $\langle BD \rangle$  of 0.3 results, highlighting the relevance of the 0.3 threshold. The relevance of this 0.3 threshold also follows from the  $\langle GD \rangle$  part in the second row, in which Structure IV is not a gradient (way too much red) and Structure V is, due to a good balance of green and red and some chain deviations. The corresponding  $\langle GD \rangle$  values are above and below 0.3.

The bottom part of Figure S13 provides analogous figures for the asymmetric contribution, focusing on the 70:30 case. The first row shows that Structure VII should be ranked as excellent and indeed the threshold value of 0.05 works. The bottom row relates to the three targets defined in the main text and the comparison of Pi vs Ti (i=1,2,3). An explicit line at  $\langle SD \rangle$  equal to 0.13 is put and is clear that only by doing so a distinction can be made between the three subplots, with for P1 only a labeling toward good and for P2 and P3 the labeling good worthy.

It should be reminded that the labeling and threshold values remains somewhat arbitrary but with more and more data available better guidelines can formulated. In any case, the qualitative trend is correct.

#### S3. Extra information for Results and Discussion

#### S3.1. Monomer conversion Profile



Fig. S14 The specific MeOx/PhOx kinetic parameters dictate a fast propagation of MeOx (Left) and a slow propagation of the PhOx monomer (Right). Significant PhOx conversions start at around a total conversion of 0.7. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

S3.2. Population fractions



Fig. S15 Mass fractions vs. overall monomer conversion for  $P_1$  (a),  $P_2$  (b) and  $P_3$  (c) chains. For the  $P_3$  product, a more efficient conversion of  $Pop_2$  into  $Pop_3$  chains can be observed. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

S3.3. Average structural deviation, method b



Fig. S16 The average structural deviation  $(\langle SD_i \rangle)$  vs. overall monomer conversion for  $P_1$ (a),  $P_2$  (b) and  $P_3$  (c) chains. The  $\langle SD_{Br} \rangle$  is calculated according to method *b*; by taking the mass average  $SD_{Br,b}$  for the three arm pairs of a single-branched species. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

S3.4. Dispersity



Fig. S17 Dispersity vs. overall monomer conversion for  $P_1$  (a),  $P_2$  (b) and  $P_3$  (c). The  $Pop_2$  chains show a much larger dispersity than the  $Pop_1$  or the  $Pop_3$  chains. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

S3.5.  $\omega$  PhOx incorporation



Fig. S18  $\omega$  PhOx incorporation vs. overall monomer conversion for  $P_1$  (a),  $P_2$  (b) and  $P_3$  (c). For  $Pop_1$  and  $Pop_3$  chains this is quasi 100%. Only the  $Pop_2$  chains struggle to incorporate the PhOx monomer sufficiently. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

S3.6. Mass average molar mass



Fig. S19 Mass average molar mass  $(M_w)$  vs. overall monomer conversion for  $P_1$  (a),  $P_2$  (b) and  $P_3$  (c) chains. For all three products, the  $Pop_2$  and  $Pop_3$  chains show a significantly different  $M_w$  from the  $Pop_1$  chains. CROP in acetonitrile at 140°C; target DP of 150; model parameters: Table 1.

#### S3.7. Temperature and target DP effect (cf. Figure 9 in the main text)

Related to Figure 9 in the main text, Figure S19 provides the variations of the mass fractions as a function of polymerization temperature and target DP. It follows that increasing the polymerization temperature results in an overall decrease of the targeted  $Pop_1$  chains.

In the investigated window of conditions, the gradient products seem more sensitive to temperature for its  $Pop_1$  fraction than the di-block products. More in detail, the gradients show a highest sensitivity to temperature within the target DP range of *ca*. 200 to 300, while the di-blocks seem more sensitive within the target DP range of *ca*. 350 to 450.



Fig. S20 Effect of the target degree of polymerization (Target DP) and the polymerization temperature for synthesis procedures of the  $P_2$  and  $P_3$  type (always 70:30 final composition), aiming at the block-gradient  $T_2$  (left) and a di-block  $T_3$  (right); Fig. 3 (d-f) explicitly show the targeted structured for the targed DP of 150 and 70:30 final composition. (a, b) the mass fraction of  $Pop_1$  ( $m_{Lin,1}$ ), (c, d) the mass fraction of  $Pop_2$ 

# $(m_{Lin,2})$ , and (e, f) the mass fraction of $Pop_3$ $(m_{Br})$ , at 0.98 overall conversion; extra info for Figure 9.

More so than the polymerization temperature, the target DP shows to be directly correlated to the fraction  $Pop_1$  chains.. Up until a DP of *ca*. 100, the formation of side products is less relevant in both structural variants of the MeOx/PhOx products.

### **S4. References**

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