Supporting Information for "Multi-angle evaluation of kinetic Monte-Carlo simulations as a tool to evaluate the distributed monomer composition in gradient copolymer synthesis"

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1 EXTRA ANALYSIS FOR IDEAL COPOLYMER SAMPLES

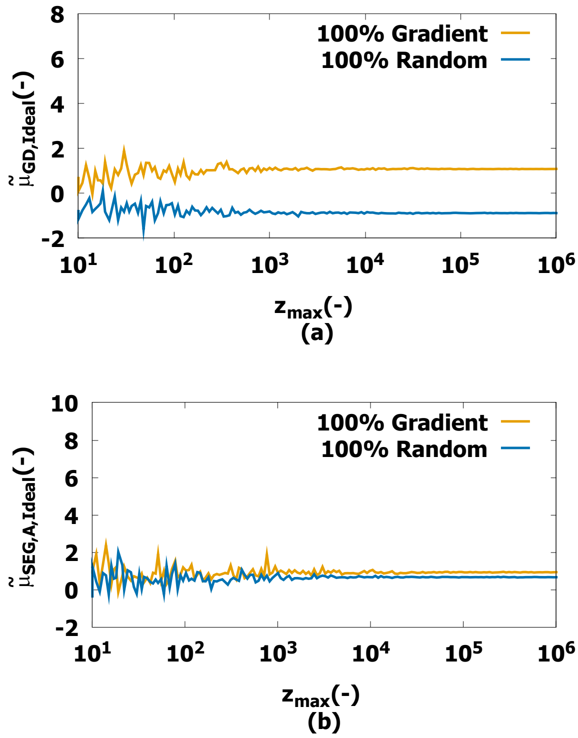

Figure S1. The skewness of a full gradient copolymer product (*cf.* P6=T1 in main text; orange lines) and of a fully randomly distributed copolymer product (*cf.* P10 in main text; blue lines) of the GD (a) and SEG_A (b) for various sample sizes. I follows that simulation size of 10^6 chains suffices to gain reliable results.

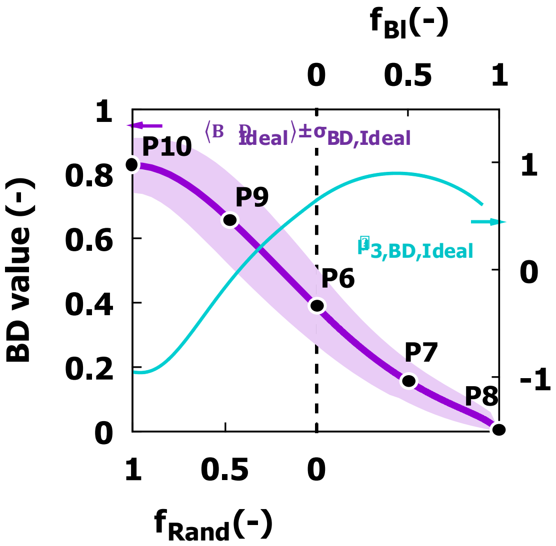

Figure S2. Transforming a targeted block structure (P8 in Figure 4(b) in the main text; f_{Gr}=0; f_{Bl}=1) into ideal gradient structures (f_{Gr}=1) or random structures (f_{Rand}=1) shows a continuous increase in the measured $\langle BD_{Ideal}\rangle \pm \sigma_{BD,Ideal}$ while also a negative skewness $\tilde{\mu}_{BD,Ideal}$ is associated with (highly) randomly distributed copolymer products. Note that for P8 a $\langle BD\rangle$ of 0 is reached as the mathematical definition of monomer inclusion probabilities include only integer numbers, which exist exclusively in a generated copolymer sample. High $\langle BD\rangle$ values, in combination with $\langle GD\rangle$ values of around 0.5, can as such be used to distinguish random or alternating structures.

2 EXTRA SIMULATION RESULTS FOR REAL CROP CONDITIONS WITHOUT SIDE REACTIONS

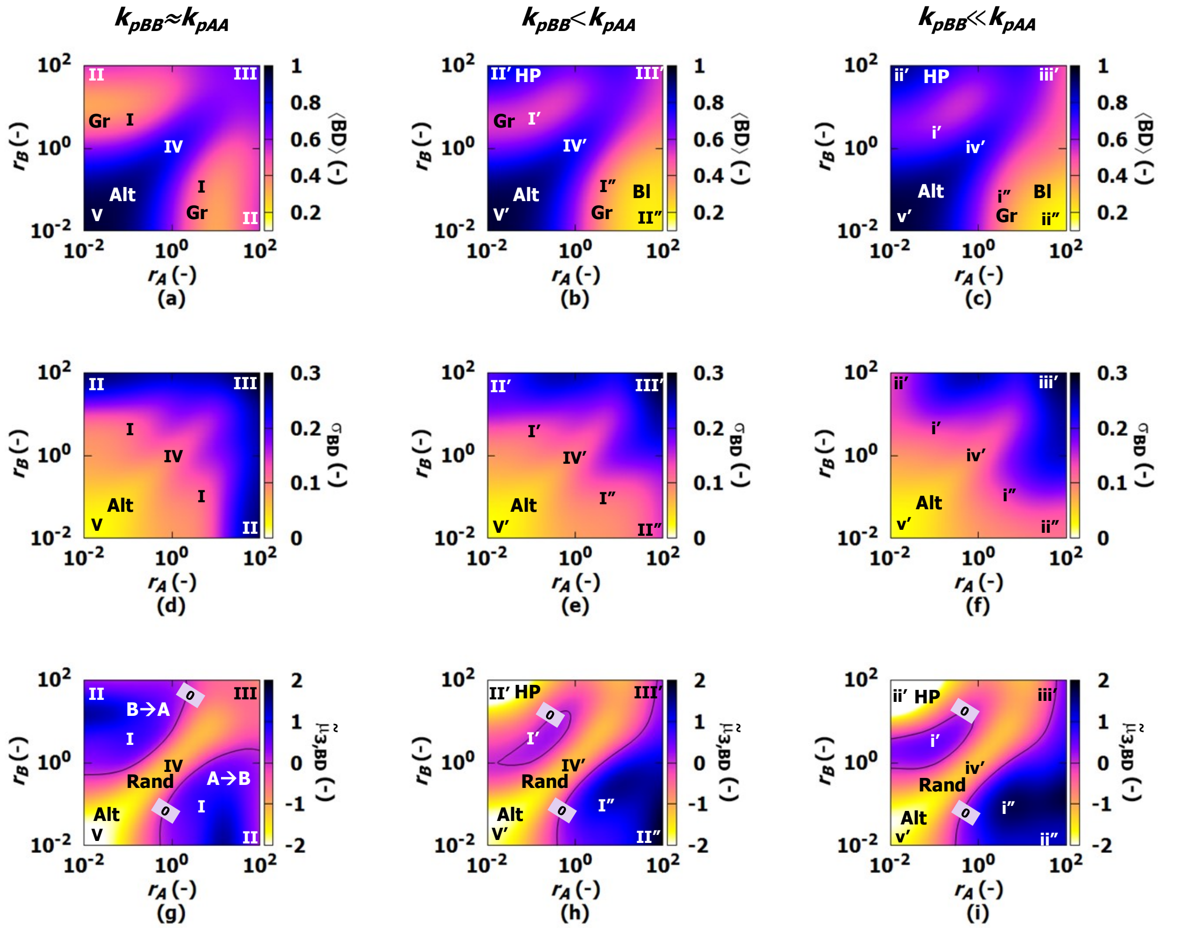

Figure S3. Extra information for Figure 5 in the main text. Relation between the (monomer) reactivity ratios r_A and r_B, and derived properties for BD distributions for CROP copolymers, according to parameters in Table 1 ($k_{i,A}$=5$k_{p,AA}$ and $k_{i,B}$=5$k_{p,BB}$; target DP=100 and B-Func=50mol%). A low $\langle BD\rangle$ (block structure) is found for copolymers with unequal homopropagation rates where $k_{p,BB}$<$k_{p,AA}$ (middle and right column) and r_B<r_A (regions II" and ii"). A low σ_{BD} indicates more chain analogy, like random or alternating copolymers where competition for other compositional distributions is less. While a positive $\tilde{\mu}_{3,BD}$ value still indicates a clear A to B shift *cf.* $\tilde{\mu}_{3,GD}$, a negative $\tilde{\mu}_{3,BD}$ can be found for homopolymeric, random and alternating copolymers but also for tapered copolymers with long segment lengths but no specific A to B transitions. Left column: equal homopropagation rate coefficients ($k_{p,BB}$=$k_{p,AA}$; case 1); middle column: slow BB-propagation ($k_{p,BB}$=0.1 $k_{p,AA}$; case 2) right column: very slow BB-propagation ($k_{p,BB}$=0.01$k_{p,AA}$). Specific counterplots also provided for P11-18 (see further).

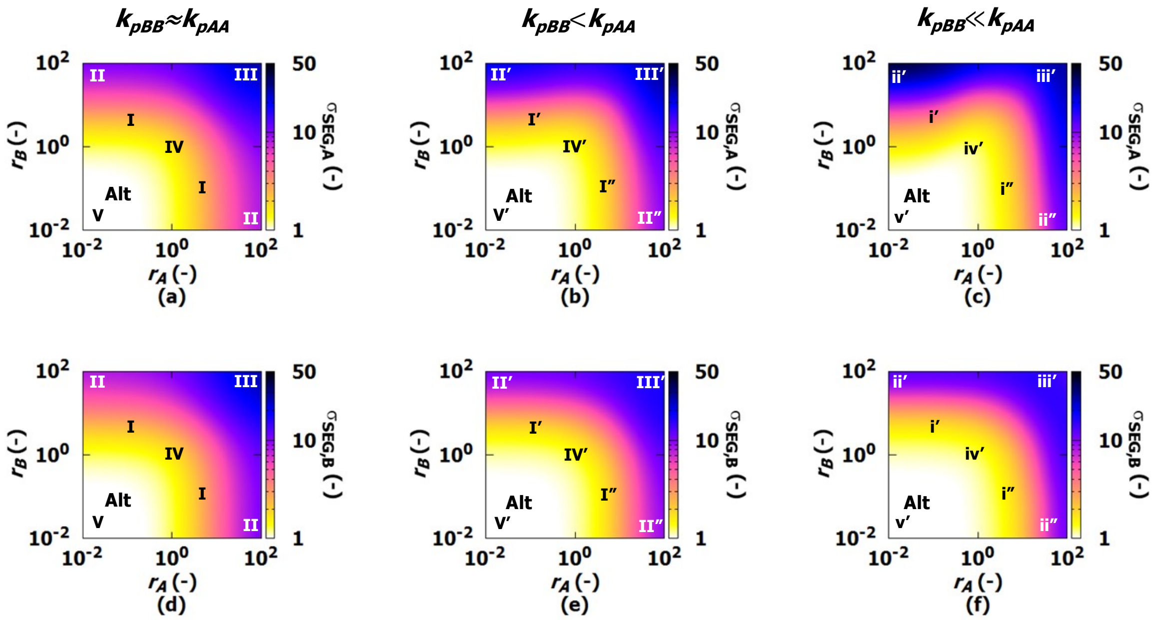

Figure S4. Complementary to Figure 6 in the main text with transitions towards non-gradient random (IV) or alternating (V) through decreased $\sigma_{SEG,A/B}$ values, and towards block (II,II',III) or homopolymeric (II,II",III) structures trough increased $\sigma_{SEG,A/B}$ values, both compared to gradient structures (I,I',I"). Counter plots for values of 2, 3, 10 and 20 also provided.

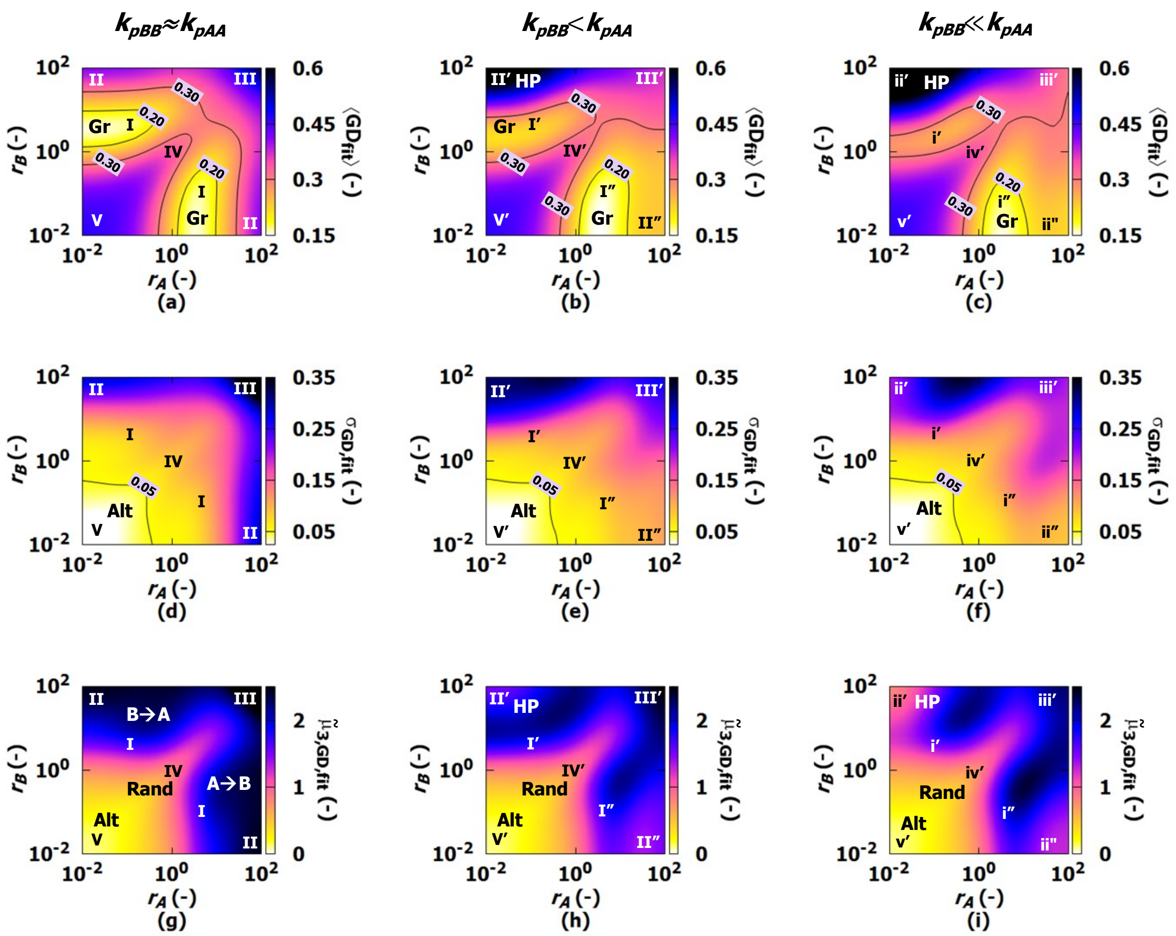

Figure S5. Extra information to Figure 5 in the main text. Relation between the reactivity ratios r_A and r_B, and the log-normally fitted GD_{fit} distributions for CROP copolymers. A low $\langle GD_{fit} \rangle$ is found for gradient structures, while high values are typical for homopolymeric chains. A low $\sigma_{GD,fit}$ indicates a well-defined structure, like random or alternating copolymers where competition for other compositional distributions is minimal. A $\tilde{\mu}_{3,GD,fit}$ is always positive with log-normal distributions always being right skewed. Random, alternating and homopolymers show negative $\tilde{\mu}_{3,GD,fit}$ positive values close to 0. Left column: equal homopropagation rate coefficients ($k_{p,BB}$=$k_{p,AA}$); right column: slow BB-propagation ($k_{p,BB}$=0.1$k_{p,AA}$). For all sets of kinetic parameters the $k_{i,A}$=5$k_{p,AA}$ and $k_{i,B}$=5$k_{p,BB}$. Initial conditions: DP 100, B-Func=50mol%.

The $\tilde{\mu}_{3,GD,fit}$ for the log-normal distribution is given by:[1]

$$\tilde{\mu}_{3,GD,fit} = \left(\exp\left(\sigma_{GD,fit}^{2}\right) + 2\right)\sqrt{\exp\left(\sigma_{GD,fit}^{2}\right) - 1} \qquad (S1)$$

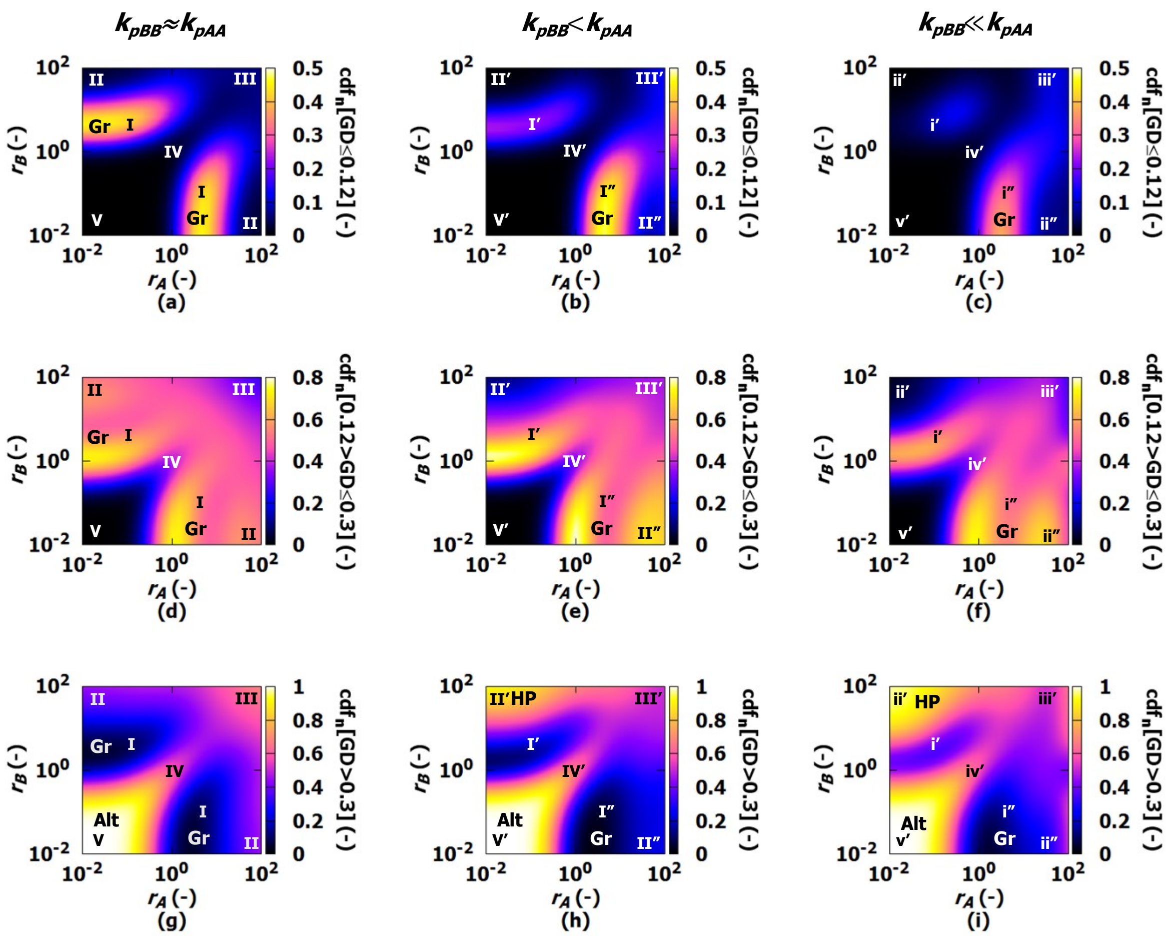

Figure S6. Original data for Figure 8 through classifying chains in a copolymer sample according to excellent, good or poor in compositional control. The threshold values are coming from previous work[2] and are the $\langle GD \rangle$ and $GD_{98\%}$ for the ideal copolymer sample generated based on the monomer inclusion probability functions.

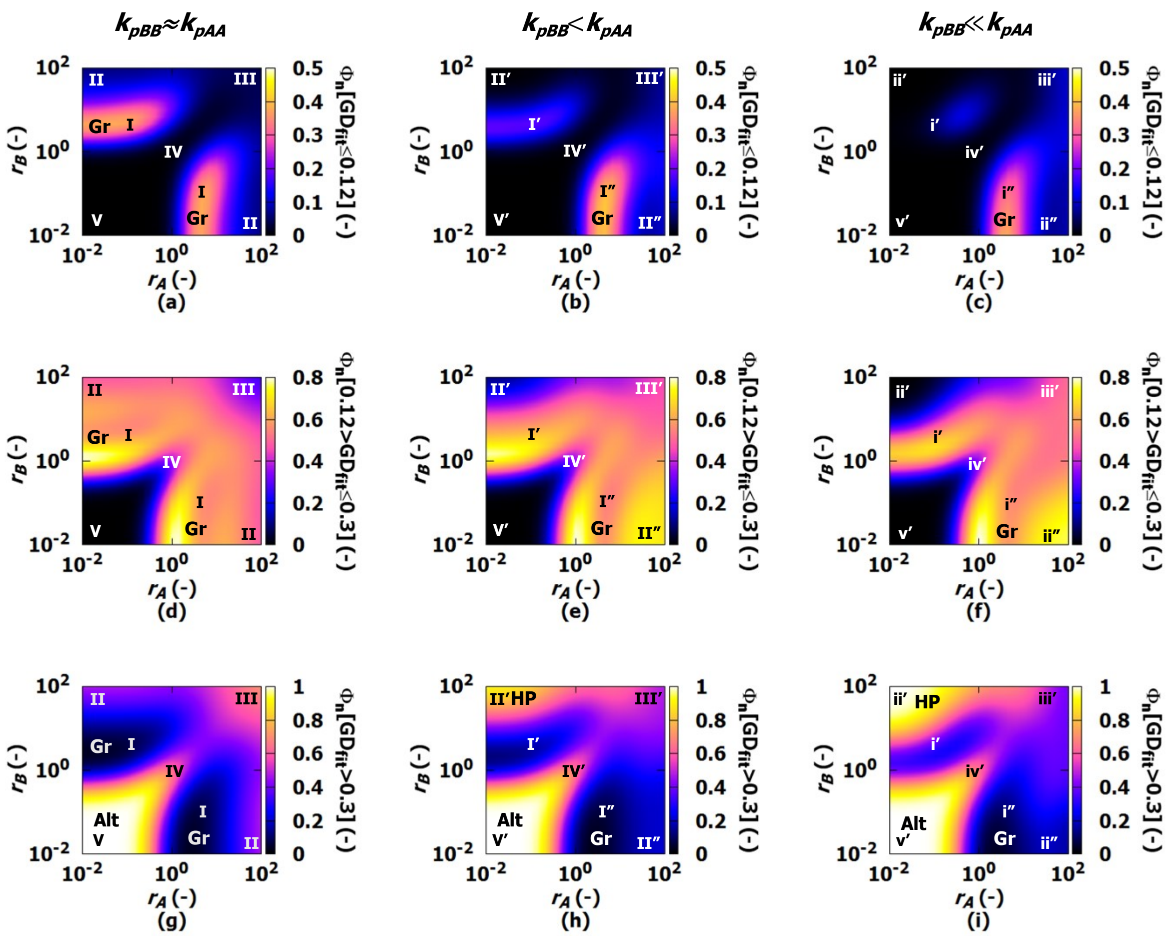

Figure S7. Relation between the reactivity ratios r_A and r_B, and the fitted GD distributions for CROP copolymers. A low $\langle GD_{fit}\rangle$ is found for gradient structures, while high values are typical for homopolymeric chains. A low $\sigma_{GD,fit}$ indicates a well-defined structure, like random or alternating copolymers where competition for other compositional distributions is minimal. A $\tilde{\mu}_{3,GD,fit}$ is always positive with log-normal distributions always being right skewed. Random, alternating and homopolymers show negative $\tilde{\mu}_{3,GD,fit}$ positive values close to 0. Left column: equal homopropagation rate coefficients ($k_{p,BB}$=$k_{p,AA}$); right column: slow BB-propagation ($k_{p,BB}$=0.1$k_{p,AA}$). For all sets of kinetic parameters the $k_{i,A}$=5$k_{p,AA}$ and $k_{i,B}$=5$k_{p,BB}$. Initial conditions: DP 100, B-Func=50mol%.

3 Extra results for real CROP and ATRP products without side reactions

Table S1. Reaction rate coefficients and monomer reactivity ratios for CROP copolymers P11-15 at 140 °C.

k (L · mol^{-1} · s^{-1})	P11	P12	P13	P14	P15
$k_{i,A}$	$1.94 \cdot 10^{-2}$[a]	$1.94 \cdot 10^{-2}$[a]	$4.65 \cdot 10^{-2}$[d]	$1.94 \cdot 10^{-2}$[a]	$4.65 \cdot 10^{-2}$[d]
$k_{i,B}$	$3.15 \cdot 10^{-3}$[a]	$3.28 \cdot 10^{-2}$[c]	$3.28 \cdot 10^{-2}$[c]	$2.86 \cdot 10^{-2}$[c]	$2.86 \cdot 10^{-2}$[c]
$k_{p,AA}$	$1.45 \cdot 10^{-1}$[b]	$1.45 \cdot 10^{-1}$[b]	$3.49 \cdot 10^{-2}$[d]	$3.49 \cdot 10^{-2}$[d]	$3.49 \cdot 10^{-2}$[d]
$k_{p,AB}$	$7.27 \cdot 10^{-2}$[a]	$4.83 \cdot 10^{-2}$[c]	$3.17 \cdot 10^{-2}$[c]	$1.32 \cdot 10^{-1}$[c]	$4.36 \cdot 10^{-2}$[c]
$k_{p,BB}$	$3.15 \cdot 10^{-2}$[b]	$6.56 \cdot 10^{-2}$[b]	$6.56 \cdot 10^{-2}$[b]	$5.71 \cdot 10^{-2}$[b]	$5.71 \cdot 10^{-2}$[b]
$k_{p,BA}$	$9.40 \cdot 10^{-1}$[a]	$3.28 \cdot 10^{-1}$[c]	$3.28 \cdot 10^{-1}$[c]	$5.71 \cdot 10^{-1}$[c]	$1.43 \cdot 10^{-1}$[c]
r_A	20[c]	3[c]	1.1[c]	1.1[c]	0.8[c]
r_B	0.03[c]	0.2[c]	0.2[c]	0.1[c]	0.4[c]
k_{trMAA}	$2.94 \cdot 10^{-4}$[e]	$2.94 \cdot 10^{-4}$[e]	$6.57 \cdot 10^{-2}$[d]	$2.94 \cdot 10^{-4}$[e]	$6.57 \cdot 10^{-2}$[d]
k_{pmAA}	$1.45 \cdot 10^{-2}$[e]	$1.45 \cdot 10^{-2}$[e]	$6.99 \cdot 10^{-2}$[d]	$1.45 \cdot 10^{-2}$[e]	$6.99 \cdot 10^{-2}$[d]
k_{pMidAA}	$1.45 \cdot 10^{-1}$[e]	$1.45 \cdot 10^{-1}$[e]	$3.49 \cdot 10^{-1}$[d]	$1.45 \cdot 10^{-1}$[e]	$3.49 \cdot 10^{-1}$[d]

[a]Taken from Van Steenberge *et al.*[3] [b]Taken from Wiesbrock *et al.*[4] [c]Taken from Bouten *et al.*[5] [d]Taken from Arraez *et al.*[6] [e]Taken from Conka *et al.*[7]

Table S2. Reaction rate coefficients and monomer reactivity ratios for ATRP copolymers P16-18 at 80 °C.

k (L · mol^{-1} · s^{-1})	P16	P17	P18
$k_{i,A}$	$2.5 \cdot 10^{5}$[a]	$2.5 \cdot 10^{5}$[a]	$3.3 \cdot 10^{3}$[a]
$k_{i,B}$	$6.5 \cdot 10^{4}$[a]	$3.3 \cdot 10^{3}$[a]	$6.5 \cdot 10^{4}$[a]
$k_{p,AA}$	$5.0 \cdot 10^{4}$[b]	$5.0 \cdot 10^{4}$[b]	$6.6 \cdot 10^{2}$[c]
$k_{p,AB}$	$1.5 \cdot 10^{5}$[d]	$1.3 \cdot 10^{6}$[e]	$3.3 \cdot 10^{3}$[e]
$k_{p,BB}$	$1.3 \cdot 10^{3}$[f]	$6.6 \cdot 10^{2}$[c]	$1.3 \cdot 10^{3}$[c]
$k_{p,BA}$	$4.3 \cdot 10^{2}$[d]	$1.1 \cdot 10^{3}$[e]	$1.6 \cdot 10^{3}$[e]
r_A	0.3[d]	0.2[e]	0.4[e]
r_B	3.0[d]	0.8[e]	0.6[e]

[a]Homopropagation rate coefficient multiplied by 5 to ensure a living polymerization character. [b]Taken from Asua *et al.*[8] [c]Taken from Buback *et al.*[9] [d]Taken from Matyjaszewski *et al.*[10] [e]Taken from Van Steenberge *et al.*[3] [f]Taken from Beuermann *et al.*[11]

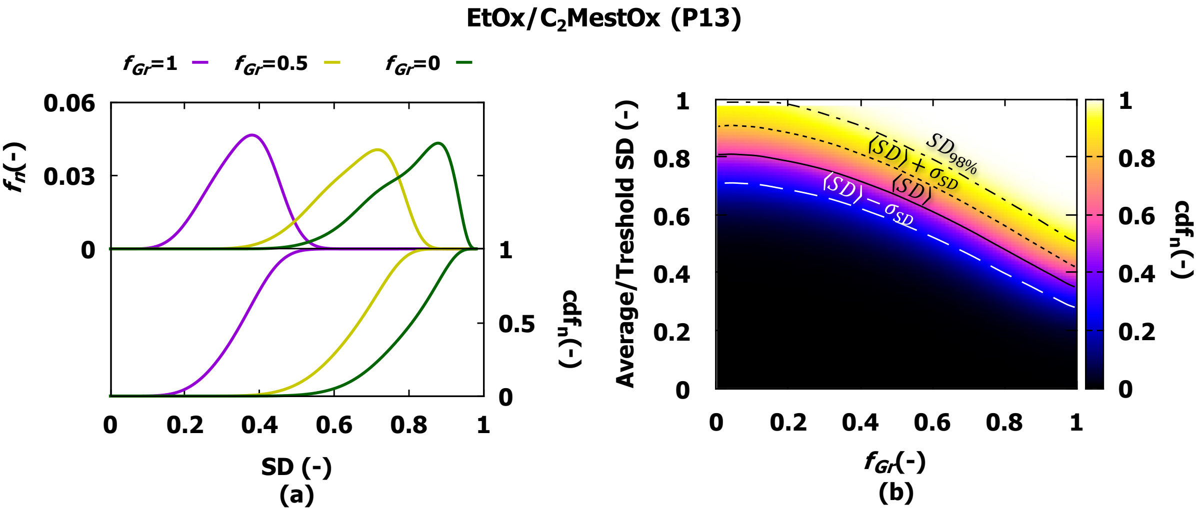

Figure S8. P13 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P13 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P13 while high SD values for f_{Gr}=0 (BD) indicate a strongly randomly distributed gradient copolymer.

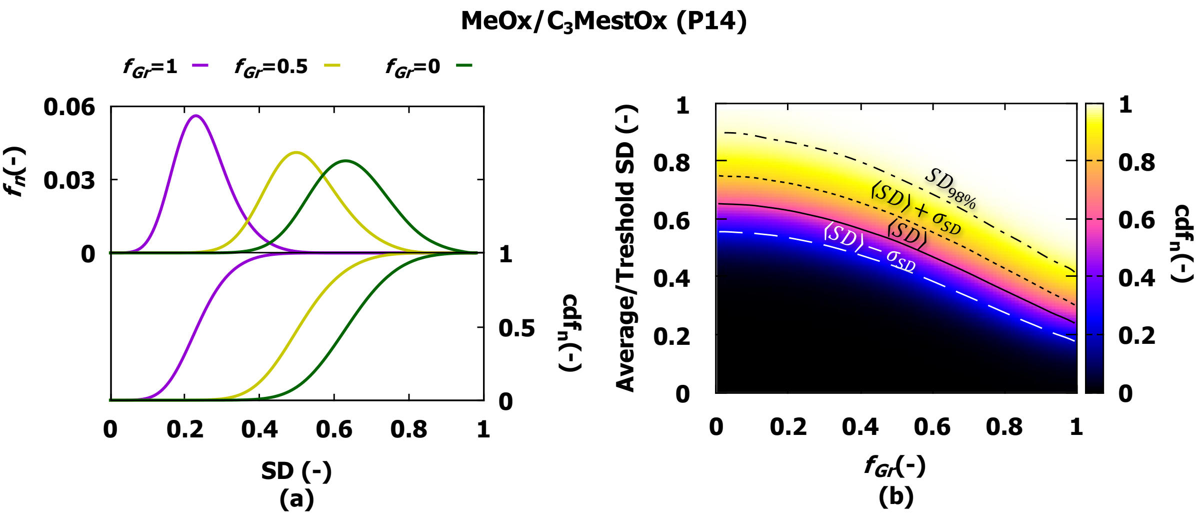

Figure S9. P14 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P14 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P14 while low SD values for f_{Gr}=0 (BD) indicate a less randomly distributed gradient copolymer.

EtOx/C$_3$MestOx (P15)

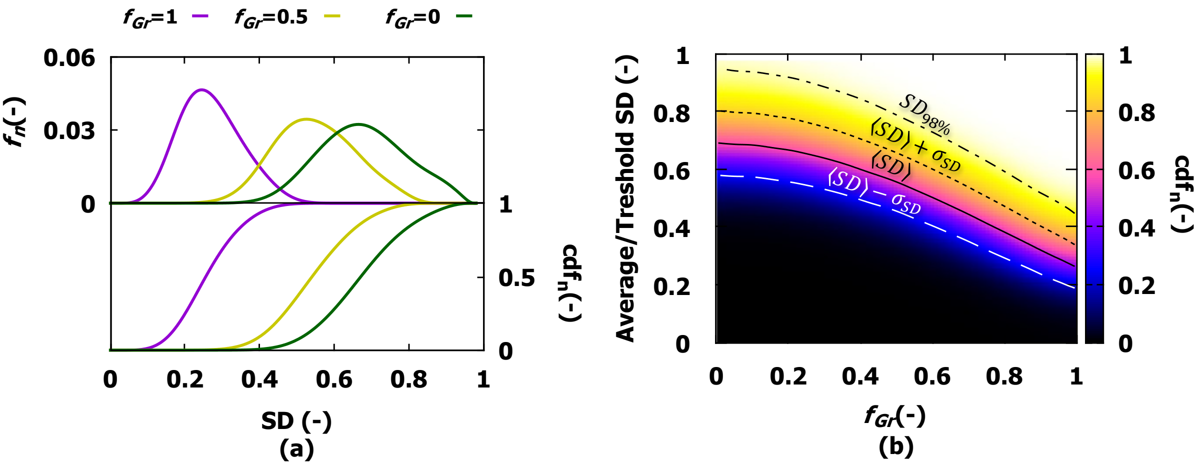

Figure S10. P15 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P15 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P15 while intermediate SD values for f_{Gr}=0 (BD) indicate a some randomness in the comonomer distribution of the gradient copolymer.

***n*BuA/MMA (P16)**

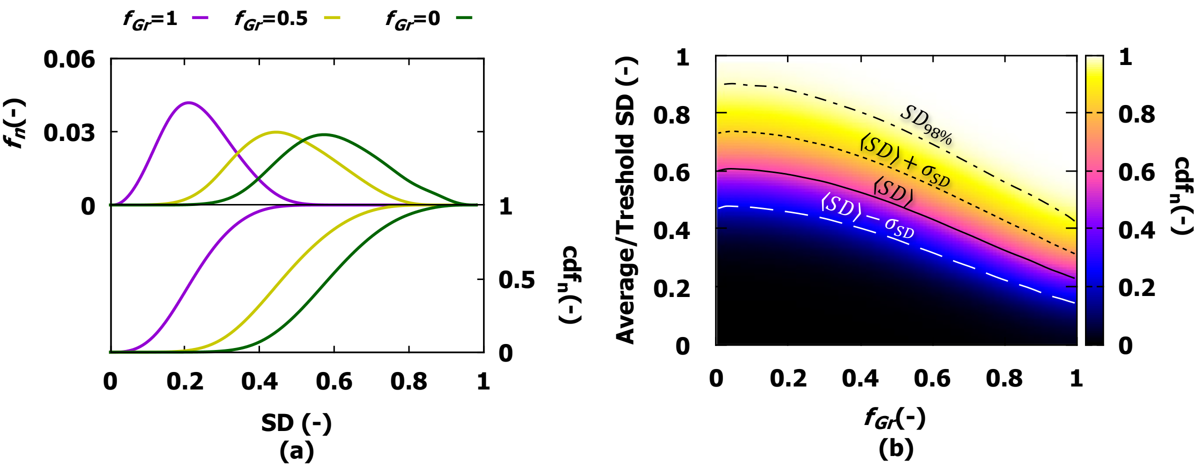

Figure S11. P16 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P16 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P16 while low SD values for f_{Gr}=0 (BD) indicate a less randomly distributed gradient copolymer.

nBuA/Sty (P17)

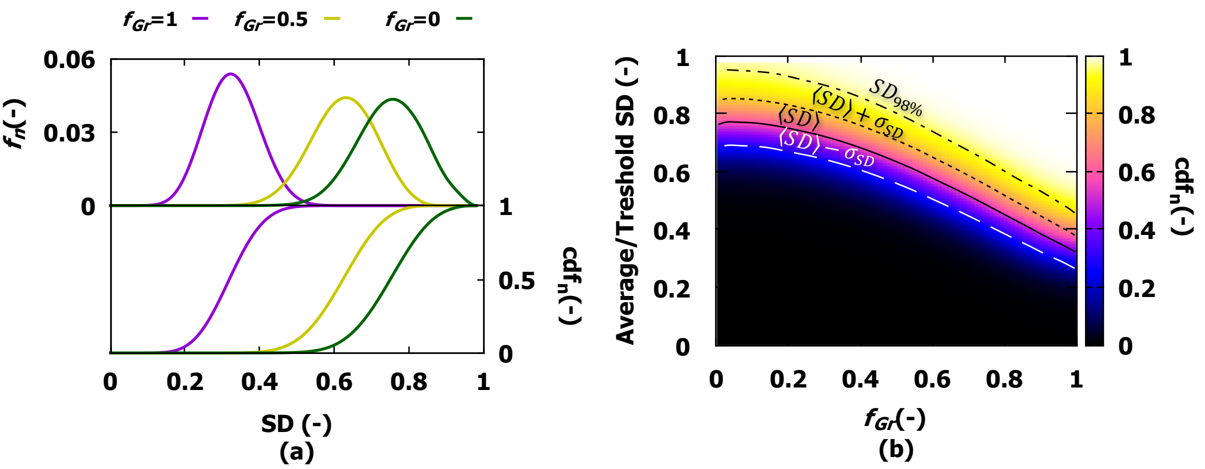

Figure S12. **P17 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P17 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P17 while high SD values for f_{Gr}=0 (BD) indicate a strongly randomly distributed gradient copolymer.**

Sty/MMA (P18)

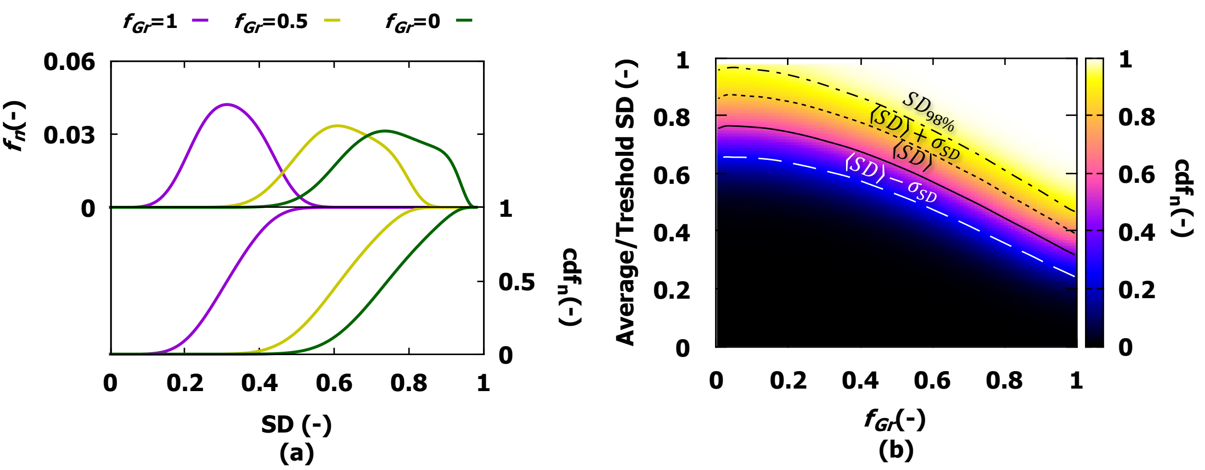

Figure S13. **P18 is compared for three selected f_{Gr} values (a; f_{Gr}=1; purple line; f_{Gr}=0.5; yellow line; f_{Gr}=0; green line). It follows that P18 is a 100 mol% gradient. (b) the cdf_n is measured for the full f_{Gr} spectrum further confirming the gradient character of P18 while high SD values for f_{Gr}=0 (BD) indicate a strongly randomly distributed gradient copolymer.**

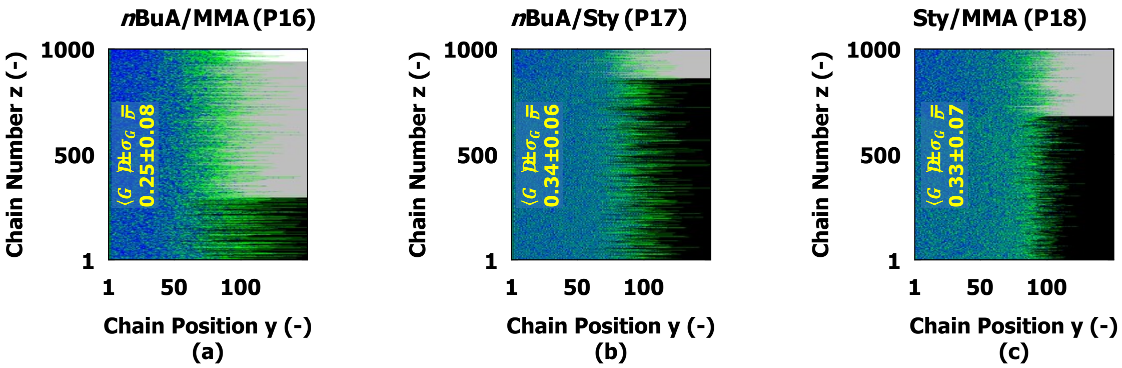

Figure S14. Monomer sequences for the f_{Gr}=1; f_{Bl}=0 A(blue)/B(green) ATRP products *n*BuA/MMA (P16; subplot (a)), *n*BuA/Sty (P17; subplot (b)), Sty/MMA (P18; subplot (c)) .

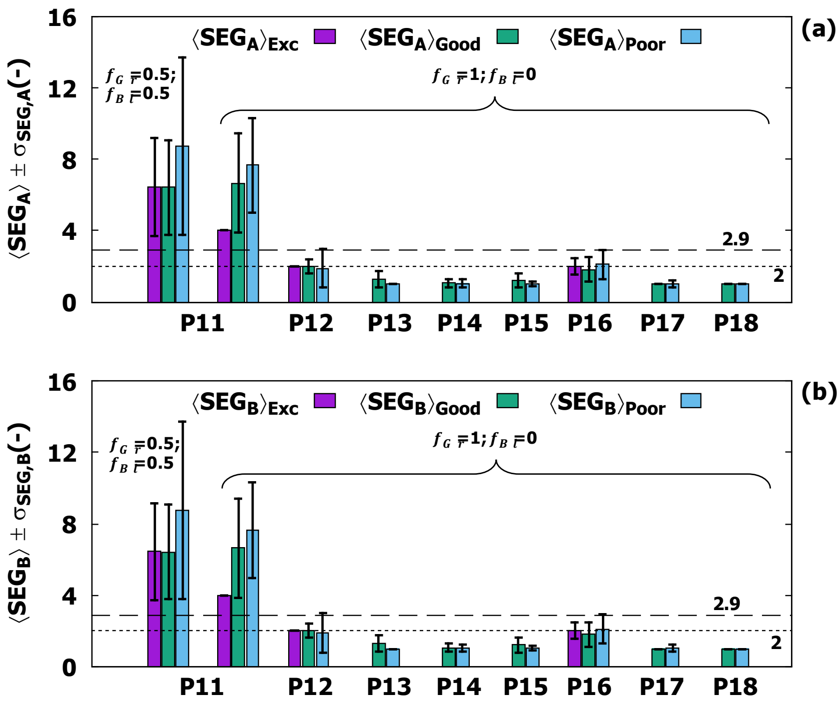

Figure S15. Decrease in structural quality from excellent (purple bars) to good (green bars) to poor (blue bars), shows an increase in $\langle SEG_A \rangle$ (a) and $\langle SEG_B \rangle$ (b) for the blocky P11 and a stagnation or even decrease in $\langle SEG_A \rangle$ (a) and $\langle SEG_B \rangle$ (b) for the more random products P12-18.

4 EXTRA RESULTS FOR REAL CROP PRODUCTS WITH SIDE REACTIONS

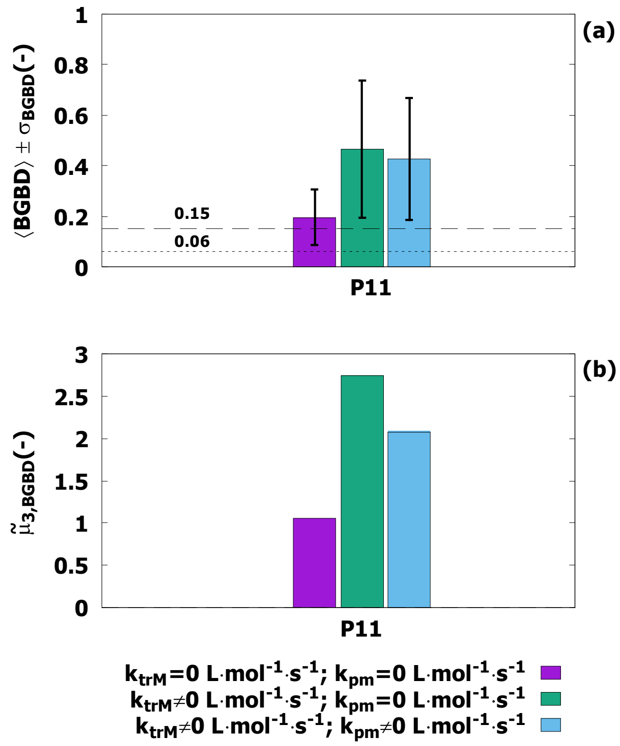

Figure S16. A histogram showing (a) $BGBD \pm \sigma_{BGBD}$ and (b) $\tilde{\mu}_{3,BGBD}$ for P11 without side reactions (purple) which leads to the targeted product exclusively, only with chain transfer to monomer (green) which also form linear side products, and with macropropagation (cyan) which also forms branched side products.

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