- SUPPORTING INFORMATION -

Poly(propylene oxide-co-ethylene oxide) gradient is controlled by the polymerization method: determination of reactivity ratios by direct comparison of copolymerization models

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Fig. S1. Proposed structure of the active site of Zn–Co(III) DMC catalyst.¹

Section S1: Derivation differential and integral equations for the non-terminal model

Transformation of the non-terminal model by Wall² into the molar fraction form:

$$\frac{d\left[\mathbf{M}_{1}\right]}{d\left[\mathbf{M}_{2}\right]} = r\frac{\left[\mathbf{M}_{1}\right]}{\left[\mathbf{M}_{2}\right]}; f = \frac{\left[\mathbf{M}_{1}\right]}{\left[\mathbf{M}_{1}\right] + \left[\mathbf{M}_{2}\right]}; F = \frac{d\left[\mathbf{M}_{1}\right]}{d\left[\mathbf{M}_{1}\right] + d\left[\mathbf{M}_{2}\right]}$$
$$F = \frac{rf}{rf - f + 1}$$

Integration of the instantaneous equation by the relation of Skeist³, gives the **ideal integrated equation** which is the central equation used in this work (in blue below):

$$\frac{df}{dX} = \frac{f - F}{1 - X} \text{ where } X = 1 - \frac{[M_1] + [M_2]}{[M_1]_0 + [M_2]_0}$$

$$\int_0^X \frac{1}{1 - X} dX = \int_{f_0}^f \frac{rf - f + 1}{rf^2 - f^2 + f - rf} df$$

$$-\log(1 - X) = \left[\frac{r\log(1 - f) - \log(f)}{r - 1}\right]_{f_0}^f$$

$$X = 1 - \left(\frac{f}{f_0}\right)^{\frac{1}{r-1}} \left(\frac{1 - f}{1 - f_0}\right)^{\frac{r}{1 - r}}$$

These equations correspond to the special case of the Mayo-Lewis⁴ and Meyer-Lowry⁵ equations for ideal behavior ($r_1 \cdot r_2 = 1$):

$$F = \frac{r_1 \cdot f^2 + f(1-f)}{r_1 \cdot f^2 + 2f(1-f) + r_2(1-f)^2}; r_2 = \frac{1}{r}; r_1 = r$$

$$F = \frac{rf}{rf - f + 1}$$

$$X = 1 - \left(\frac{f}{f_0}\right)^{\frac{r_2}{1-r_2}} \cdot \left(\frac{1-f}{1-f_0}\right)^{\frac{r_1}{1-r_1}} \cdot \left(\frac{f - \frac{1-r_2}{2-r_1 - r_2}}{f_0 - \frac{1-r_2}{2-r_1 - r_2}}\right)^{\frac{r_1r_2 - 1}{(1-r_1)(1-r_2)}}; r_2 = \frac{1}{r}; r_1 = r$$

$$X = 1 - \left(\frac{f}{f_0}\right)^{\frac{1}{r-1}} \cdot \left(\frac{1-f}{1-f_0}\right)^{\frac{r_1}{1-r_1}}$$

All fits were performed using weights proportional to the total monomer concentration.

When considering copolymerization there is even a simpler possible model, which can accurately describe perfectly ideal random copolymerization, where both monomers have the same reactivity:

$$\frac{d\left[\mathbf{M}_{1}\right]}{d\left[\mathbf{M}_{2}\right]} = \frac{\left[\mathbf{M}_{1}\right]}{\left[\mathbf{M}_{2}\right]}; f = \frac{\left[\mathbf{M}_{1}\right]}{\left[\mathbf{M}_{1}\right] + \left[\mathbf{M}_{2}\right]}; F = \frac{d\left[\mathbf{M}_{1}\right]}{d\left[\mathbf{M}_{1}\right] + d\left[\mathbf{M}_{2}\right]}$$

$$F = f$$

For this model the integration by Skeist is trivial and shows the independence of the molar composition f from the conversion. This model might be applied in cases where values $r_1=r_2=1$ are expected.

$$\frac{df}{dX} = \frac{f - F}{1 - X} \text{ where } X = 1 - \frac{\left[M_1\right] + \left[M_2\right]}{\left[M_1\right]_0 + \left[M_2\right]_0}$$
$$\frac{df}{dX} = \frac{f - F}{1 - X} = 0;$$
$$f(X) = f_0$$

It should be noted that the Skeist relation can also be solved numerically which has been done for the Mayo-Lewis model and more elaborate models.⁶

Section S2: Effect of a constant factor *c* on the non-terminal and terminal model

A constant factor *c* does not change the ideal copolymerization equation:

$$\frac{x_1}{x_2} = c \frac{\left[M_1\right]}{\left[M_2\right]} \Rightarrow \frac{\left[M_1\right]}{\left[M_2\right]} = \frac{f_x}{c - cf_x}; \frac{dx_1}{dx_2} = c \frac{d\left[M_1\right]}{d\left[M_2\right]} \Rightarrow \frac{d\left[M_1\right]}{d\left[M_2\right]} = \frac{F_x}{c - cF_x}$$

$$\frac{d\left[M_1\right]}{d\left[M_2\right]} = r \frac{\left[M_1\right]}{\left[M_2\right]}$$

$$F_x = \frac{rf_x}{rf_x - f_x + 1}$$

As a result, the mole fraction can be exchanged for any other fraction with proportional ratios, e.g. weight fraction or volume fraction may also be used.

This independence of a factor c is not the case for the terminal model, which is altered by a constant factor c, as shown in the following:

$$\frac{x_{1}}{x_{2}} = c \frac{[M_{1}]}{[M_{2}]} \Rightarrow \frac{f_{x}}{c - cf_{x}} = \frac{[M_{1}]}{[M_{2}]}; \ c \frac{d [M_{1}]}{d [M_{2}]} \Rightarrow \frac{d [M_{1}]}{d [M_{2}]} = \frac{F_{x}}{c - cF_{x}}$$

$$\frac{dM_{1}}{dM_{2}} = \frac{r_{1} \frac{[M_{1}]}{[M_{2}]} + 1}{r_{2} \frac{[M_{2}]}{[M_{1}]} + 1} = \frac{F_{x}}{c - cF_{x}} = \frac{\frac{r_{1}f_{x} + c - cf_{x}}{c - cf_{x}}}{\frac{r_{2}c - cf_{x}}{f_{x}}}$$

$$F_{x} = \frac{r_{1}f_{x}^{2} + cf_{x}(1 - f_{x})}{r_{1}f_{x}^{2} + (c + 1)f_{x}(1 - f_{x}) + r_{2}c(1 - f_{x})^{2}}$$

Integration of this equation with the relation of Skeist³ yields the following equation. Note that the factor *c* only appears in the last term, which accounts for non-ideal behavior. *c* is eliminated in the ideal case $r_1=1/r_2$.

$$\frac{df_x}{dX} = \frac{f_x - F_x}{1 - X}$$
$$X = 1 - \left(\frac{f_x}{f_{x,0}}\right)^{\frac{r_2}{1 - r_2}} \cdot \left(\frac{1 - f_x}{1 - f_{x,0}}\right)^{\frac{r_1}{1 - r_1}} \cdot \left(\frac{f_x - \frac{c(1 - r_2)}{c(1 - r_2) + 1 - r_1}}{f_{x,0} - \frac{c(1 - r_2)}{c(1 - r_2) + 1 - r_1}}\right)^{\frac{r_1r_2 - 1}{(1 - r_1)(1 - r_2)}}$$



Fig. S2. Simulated data with addition of a systematic error fitted by the non-terminal Ideal Integrated (II) fit and terminal Meyer-Lowry (ML) fit.



Fig. S3. Simulated data with subtraction of a systematic error fitted by the non-terminal Ideal Integrated (II) fit and terminal Meyer-Lowry (ML) fit.



Fig. S4. Simulated data with an added (left) or subtracted (right) systematic error with Jaacks-fit.

Systematic error added		Ideal Integrated		Meyer Lowry		Jaacks	
		r _B	r _A	r _B	r _A	r _B	r _A
No error		0.33	3.0	0.33	3.0	0.33	3.0
[M _A]+0.014[M _A] ₀	absolute values	0.35	2.9	0.53	3.3	0.36	2.7
	relative error	5%	4%	59%	9%	9%	9%
[M _A]-0.014[M _A] ₀	absolute values	0.32	3.1	0.22	2.9	0.31	3.2
	relative error	4%	4%	34%	4%	7%	7%

 Table S1. Summarized results of fits of the data with systematic errors.



Fig. S5. Jaacks-fit of fit with corresponding reactivity ratios, left: monomer-activated AROP, right: DMC.

Table S2. Reactivity ratios obtained for the copolymerization of PO and EO system under different polymerization conditions.

Polymerization conditions	Ideal integrated		Jaacks ⁷		k_1/k_2	
	r _{PO}	r _{EO}	r _{PO}	r _{EO}	r _{PO}	r _{EO}
DMC catalysis	2.4	0.42	2.2	0.46	2.0	0.49
Monomer activated AROP	0.16	6.4	0.15	6.6	0.15	6.5



Fig. S6. Monomer concentration as a function of time, left: monomer-activated AROP, right: DMC catalysis.



Fig. S7. SEC traces (DMF, PEG-calibration) of P(PO-*co*-EO) copolymers from the *in situ* ¹H NMR kinetic experiments.



Fig. S8. ¹H NMR (C₆ D_6) spectra of copolymerization mixture (at 70 °C) before (top) and after (bottom) copolymerization experiment. The integrals show that the initial recorded monomer composition equals the final copolymer composition $f_{\rm EO} = F_{\rm EO} = 34\%$.

Section S3: Pseudo code for Monte Carlo simulation

First the reactivity ratios r_A and r_B are set to the chosen values. $f_{A,0}$ is set to the initial fraction of monomer A. Each simulation is performed with 10⁶ chains (n_{chains}). The total number of monomer molecules is set to the number of chains multiplied with the degree of polymerization (*DP*).

$$n_{chains} = 10^{6}$$

$$n_{A} = n_{chains} \cdot DP \cdot f_{A,0}$$

$$n_{B} = n_{chains} \cdot DP \cdot (1 - f_{A,0})$$

A chain *k* is randomly selected.

If the chain k has DP = 0, then:

A random number w in the interval [0,1] is created and the probability of incorporation of A is calculated with the Mayo-Lewis equation: $F_A = \frac{r_A f_A^2 + f(1 - f_A)}{r_A f_A^2 + 2 f_A (1 - f_A) + r_B (1 - f_A)^2}$

If F > w then add monomer A to the chain, otherwise monomer B.

If chain k has a DP > 0, then:

A random number w in the interval [0,1] is created. The monomer at the chain end k is called e. The reactivity ratio corresponding to this chain end k is used to calculate the $r_e f_e$

probability of addition of same monomer as *e*: $F_e = \frac{r_e f_e}{r_e f_e - f_e + 1}$

If $F_e > w$, then add monomer equal to e, otherwise use the monomer unequal to the chain end.

Then the number of consumed monomers n_x is reduced by 1. Then go to the step, where the next chain k is randomly selected. These steps are repeated until all monomer is consumed. Then the number of chain ends with monomer A and B are summed up to determine the fraction of chain ends with monomer A attached.

Table S3. Content of terminal primary hydroxyl groups obtained from simulation for copolymerization of PO and EO for ratios of 10:90 and 20:80, respectively, for different molecular weights by kinetic Monte Carlo simulation.

$\mathbf{M}_{\mathbf{N}}$	10% EO	20% EO	20% EO	
	(DMC)	(DMC)	(AROP)	
1000	37%	60%	0%	
2000	49%	73%	0%	
3000	57%	80%	0%	
4000	63%	84%	0%	
5000	67%	87%	0%	
6000	70%	89%	0%	
7000	73%	91%	0%	
8000	75%	92%	0%	
9000	77%	93%	0%	
10000	79%	94%	0%	



Fig. S9. Copolymer microstructure of P(PO-*co*-EO) statistical copolymers with an EO-content of 10% and 20%, synthesized by DMC catalysis (left) or AROP (right). PO is depicted in red and EO is given in blue. Due to the living nature of the copolymerization, the conversion mirrors the monomer gradient in the chains.

References

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