

Supporting Information

Towards bio-based tapered block copolymers: the behaviour of myrcene in the statistical anionic copolymerisation

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Comparison of kinetic models

In 1941 Wall introduced the first model to describe copolymerisations.¹ The Mayo-Lewis model was developed a few years later and made it possible to describe non-ideal behaviour. This extension was necessary to describe alternating copolymerisation behaviour as observed in the radical copolymerization of styrene and methyl methacrylate.² Both models are identical for the case of $r_1 \cdot r_2 = 1$. For high conversion the integrated form of the Mayo-Lewis model is necessary to accurately describe the copolymerization.² The integration can be performed by the Skeist relation.³ In this way the Meyer-Lowry equation was derived (**Table S1 Entry 3**).⁴ Recently our group derived an analogous equation for the ideal Wall Model (**Table S1 Entry 3**).⁵ In the following, the two models in differential and integral form are summarized:

Table S1 Summary and comparison of the kinetic models of Wall and Mayo and Lewis.

Entry	Non-terminal (ideal) model (Wall) ¹	Terminal model (Mayo-Lewis) ²
Differential form		
1	$\frac{dM_1}{dM_2} = r \frac{M_1}{M_2}$	$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$
Differential form in molar fraction form with $f = \frac{M_1}{M_1 + M_2}$ and $F = \frac{dM_1}{dM_1 + dM_2}$		
2	$F = \frac{rf}{rf - f + 1}$	$F = \frac{r_1 \cdot f^2 + f(1-f)}{r_1 \cdot f^2 + 2f(1-f) + r_2(1-f)^2}$
Integrated of differential fractional form with Skeist ³ relation: $\frac{df_x}{dX} = \frac{f_x - F_x}{1 - X}$		
with $X = 1 - \frac{[A] + [B]}{[A_0] + [B_0]}$		
3	$X = 1 - \left(\frac{f}{f_0}\right)^{\frac{1}{r-1}} \cdot \left(\frac{1-f}{1-f_0}\right)^{\frac{r}{1-r}}$ Integrated ideal equation ⁵	$X = 1 - \left(\frac{f}{f_0}\right)^{\frac{r_2}{1-r_2}} \cdot \left(\frac{1-f}{1-f_0}\right)^{\frac{r_1}{1-r_1}} \cdot \left(\frac{f - \frac{1-r_2}{2-r_1-r_2}}{f_0 - \frac{1-r_2}{2-r_1-r_2}}\right)^{\frac{1-r_1 r_2}{(1-r_1)(1-r_2)}}$ Meyer-Lowry equation ⁴

The integrated form of both models was used to fit the experimental data of the copolymerisation experiments. As recently described by our group, overfitting in the analysis of reactivity ratios is a problem which was not taken into account so far. Overfitting is a statistical phenomenon that occurs when data is fitted to a model which is more complex than it needs to be. This is the case when a model with more parameters than necessary is used to explain the variation in the data. The use of a model with irrelevant parameters gives a worse description of the behaviour, since the parameters are fitted to random variation (noise).⁶ Following the principle of Ockham's razor the simplest model that successfully describes the data should be used.⁷ In the case of reactivity ratios the simple Wall-Model requires just one reactivity parameter ($r_2 = \frac{1}{r_1}$) for the description of copolymerisation data, while the Mayo-Lewis model relies on two independent reactivity ratios. In the case of an ideal copolymerization r_2 is completely described as r_1^{-1} , making the independent determination of both parameters redundant. Lynd and coworkers showed that many ionic copolymerisations can be described with the ideal model, however the equation did not allow the direct comparison of the ideal model with the terminal Mayo Lewis model.⁸ The “ideal integrated” equation can be directly compared to the fit of the more elaborated terminal model (Meyer-Lowry equation) (**Figure S1, S2 and S3**).

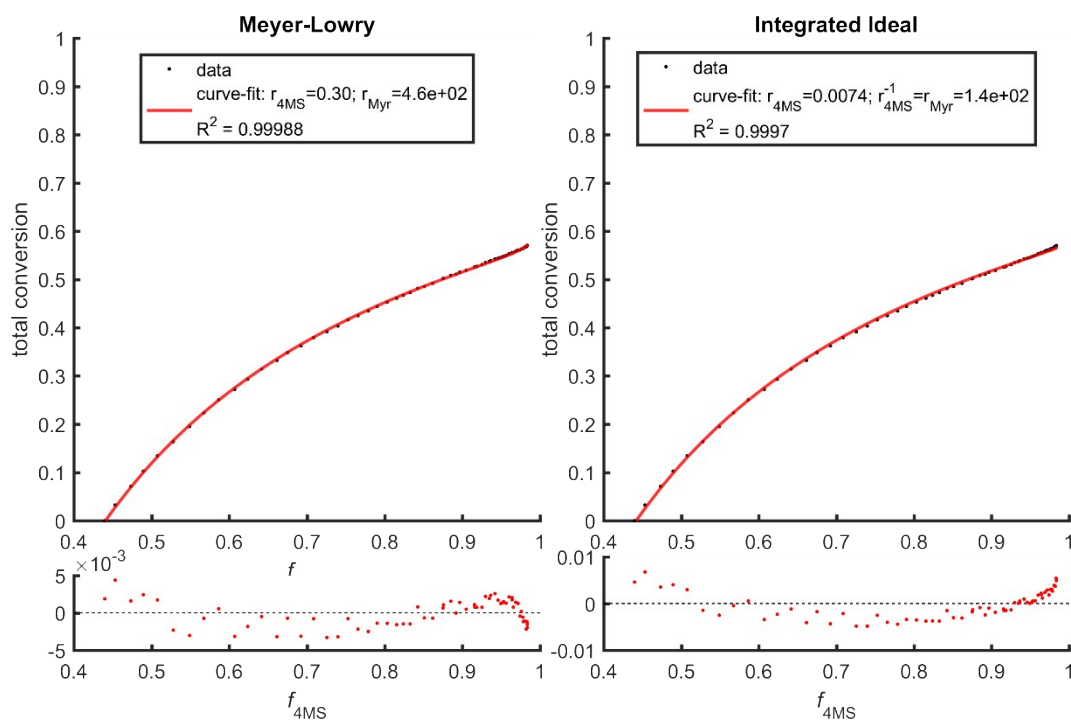


Figure S1 Comparison of the Meyer-Lowry evaluation and the integrated Ideal Model for the copolymerisation of myrcene (Myr) and 4-methylstyrene (4MS).

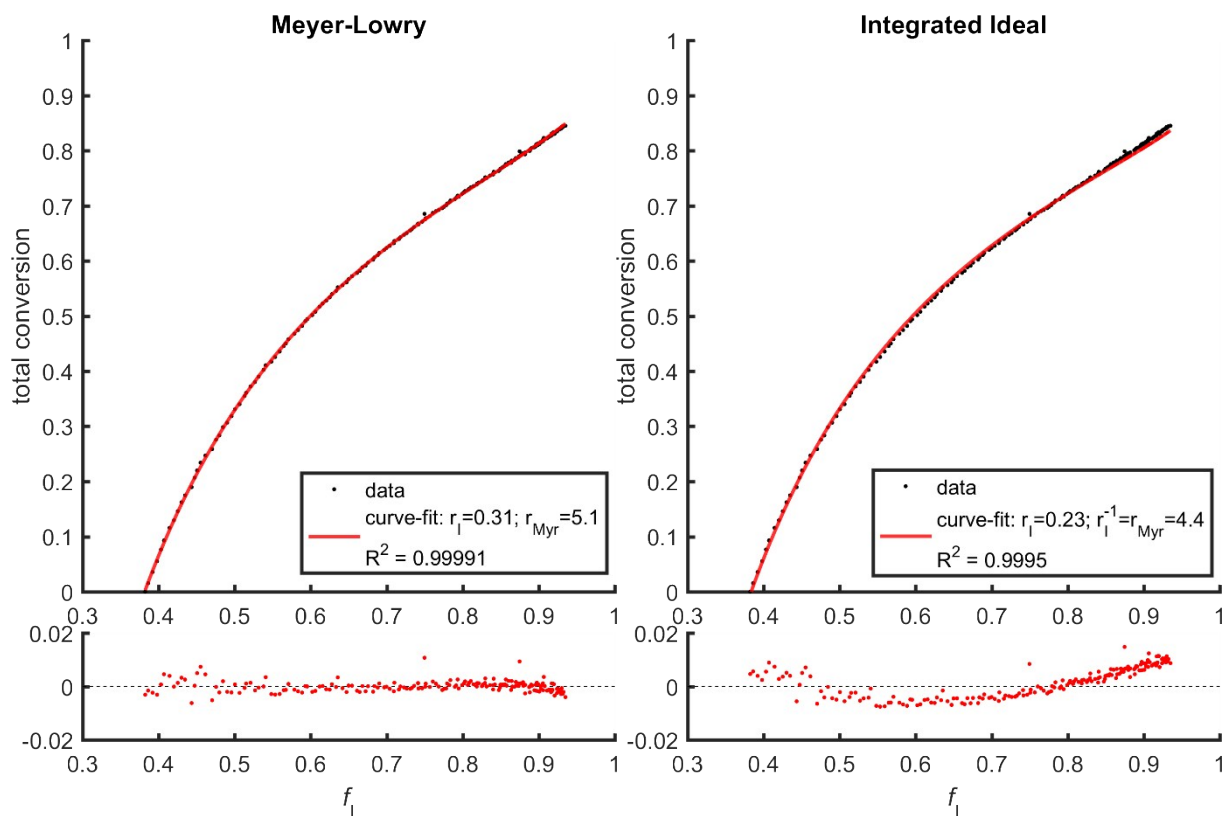


Figure S2 Comparison of the Meyer-Lowry evaluation and the integrated Ideal Model for the copolymerisation of myrcene (Myr) and isoprene (I).

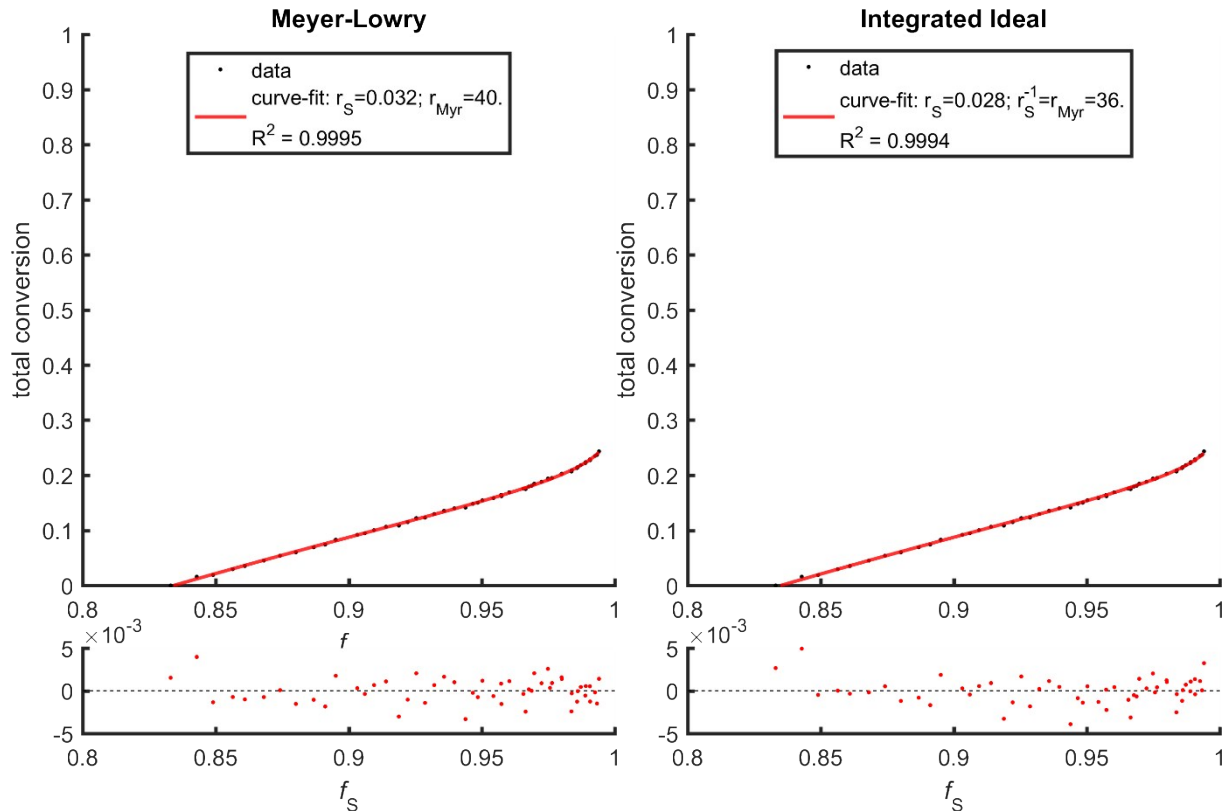


Figure S3 Comparison of the Meyer-Lowry evaluation and the integrated Ideal Model for the copolymerisation of myrcene (Myr) and styrene (S).

The results of the fits of both models to the data of the three copolymerisation experiments are shown in **Figures S1, S2 and S3**. As is evident, the Integrated ideal fit can very well describe the experimental data, and the more elaborate Meyer-Lowry fit negligibly increases the quality of the fit. This lends strong support to ideal copolymerization behaviour.

Description of the terpolymerisation of Myr/I/4MS

For the accurate description of a terpolymerisation by the non-ideal Mayo-Lewis model seven independent reactivity parameters are required.⁹ However, in the ideal case only the decrease of the three monomers (myrcene, isoprene and 4-methylstyrene) is taken into account (active chain end has no influence), and a terpolymerisation can be easily described as two simultaneous copolymerisations. From two reactivity ratios in the ideal case all other can be derived as shown in (1 and 2). The ideal behaviour can be confirmed by the pairwise fitting of the ideal model to the data of the terpolymerisation experiment. The results of these fits are shown in **Figures S4, S5 and S6** and confirm this conjecture.

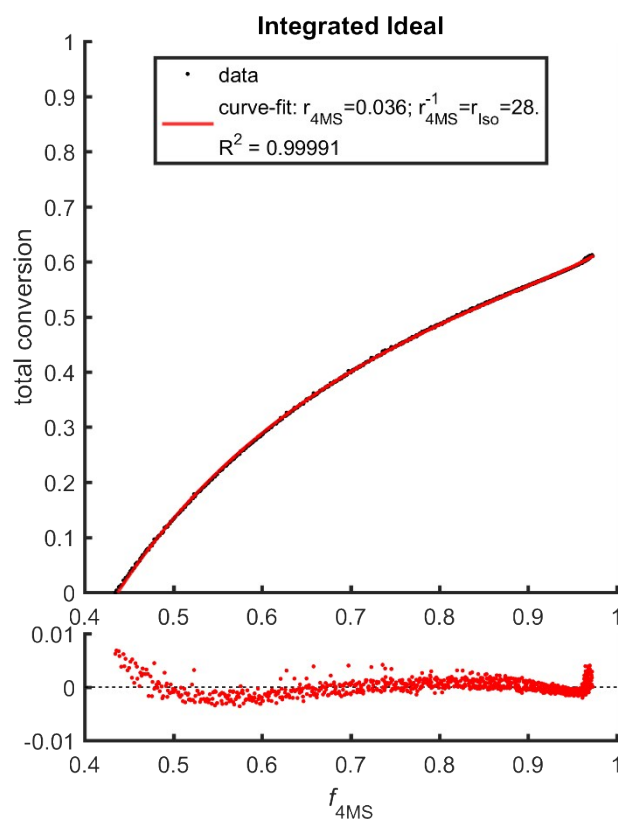


Figure S4 Pairwise Ideal Integrated Model of 4MS and I for the terpolymerisation of Myr/I/4MS.

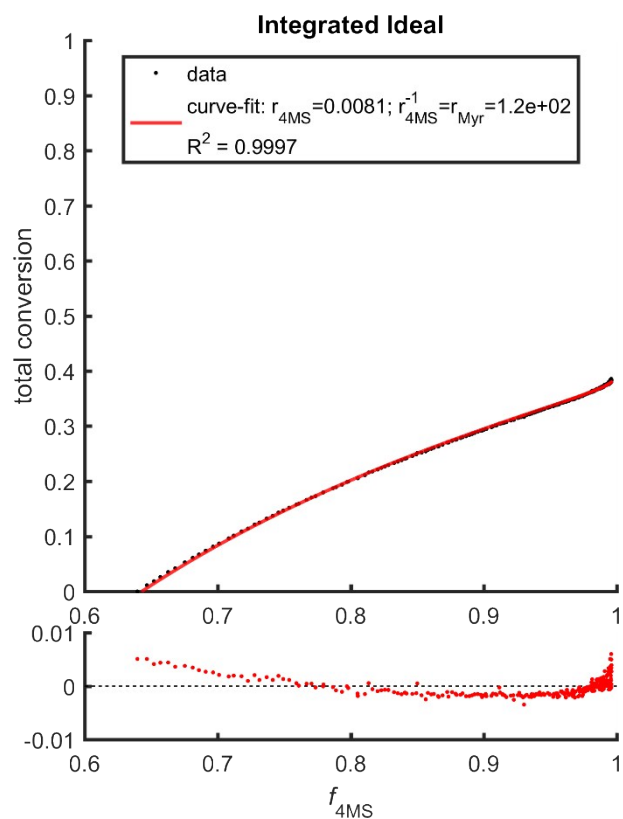


Figure S5 Pairwise Ideal Integrated Model of Myr and 4MS for the terpolymerisation of Myr/I/4MS.

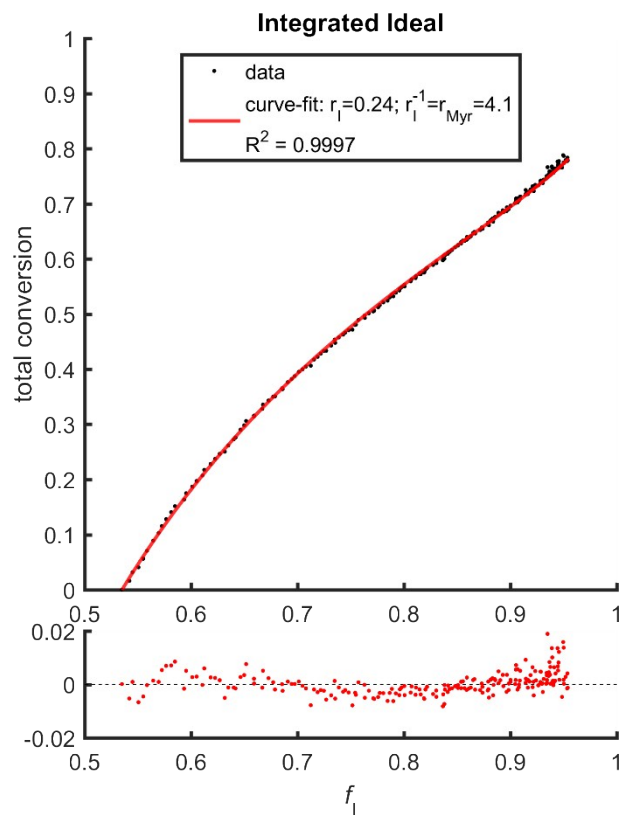


Figure S6 Pairwise Ideal Integrated model of Myr and I regarding terpolymerisation of Myr/I/4MS.

This shows that the terpolymerisation can be well-described with ideal behaviour. Another property of an ideal copolymerisation is the fact that reactivity ratios are multiplicative:

$$r_{A/B} = \frac{k_A}{k_B}; r_{A/C} = \frac{k_A}{k_C}; r_{A/A} = r_{A/B}^{-1} \quad (1)$$

$$r_{A/B} = r_{B/A} \cdot r_{A/C} = \frac{k_B}{k_A} \cdot \frac{k_A}{k_C} = \frac{k_B}{k_C} = r_{C/C} \quad (2)$$

To model the terpolymer microstructure, we chose the following approach: using the Wall model, every monomer concentration can be expressed as a function of the concentration of monomer A.

$$\frac{d[A]}{d[B]} = r_{A/B} \frac{[A]}{[B]} \Rightarrow \frac{[A]}{[A_0]} = \left(\frac{[B]}{[B_0]} \right)^{r_{A/B}} \quad (3)$$

$$[B] = [B_0] \left(\frac{[A]}{[A_0]} \right)^{r_{B/A}} \quad (4)$$

$$[C] = [C] \left(\frac{[A]}{[A_0]} \right)^{r_{A/C}} \quad (5)$$

Monomer A is set as the reference monomer. It is favourable to choose the least reactive monomer, because its concentration is non-zero throughout the whole polymerisation and approaches 0 only at full monomer conversion. An array for Monomer A is created with values in the interval $[0, [A_0]]$. The values for the arrays for B and C can be calculated from the equations (4, 5) above.

From the data for all monomers the array for the total conversion can be calculated:

$$X = 1 - \frac{[A] + [B] + [C]}{[A_0] + [B_0] + [C_0]} \quad (6)$$

In analogy the instantaneous incorporation of monomer A was calculated from the following relation:

$$\frac{d[A]}{d[A]} = 1; \frac{d[B]}{d[A]} = r_{B/A} \frac{[B]}{[A]}; \frac{d[C]}{d[A]} = r_{C/A} \frac{[C]}{[A]} \quad (7)$$

$$\frac{d[B]}{d[A]} + \frac{d[C]}{d[A]} + \frac{d[A]}{d[A]} = r_{B/A} \frac{[B]}{[A]} + r_{C/A} \frac{[C]}{[A]} + 1 \quad (8)$$

$$\frac{d[A] + d[B] + d[C]}{d[A]} = \frac{r_{B/A}[B] + r_{C/A}[C] + [A]}{[A]} \quad (9)$$

$$F_A = \frac{d[A]}{d[A] + d[B] + d[C]} = \frac{[A]}{[A] + r_{B/A}[B] + r_{C/A}[C]} \quad (10)$$

Analogously follows for the instantaneous incorporation for B and C:

$$F_B = \frac{d[B]}{d[A] + d[B] + d[C]} = \frac{r_{B/A}[B]}{[A] + r_{B/A}[B] + r_{C/A}[C]} \quad (11)$$

$$F_C = \frac{d[C]}{d[A] + d[B] + d[C]} = \frac{r_{C/A}[C]}{[A] + r_{B/A}[B] + r_{C/A}[C]} \quad (12)$$

F_A , F_B and F_C are calculated for all values in the arrays. Note that $F_A + F_B + F_C$ always yield 1 at every point. For better visualisation it is favourable to plot F_A and $F_A + F_B$ as a function of X (F_C corresponds to the distance of $F_A + F_B$ to value 1). This representation is shown in **Figure S7**.

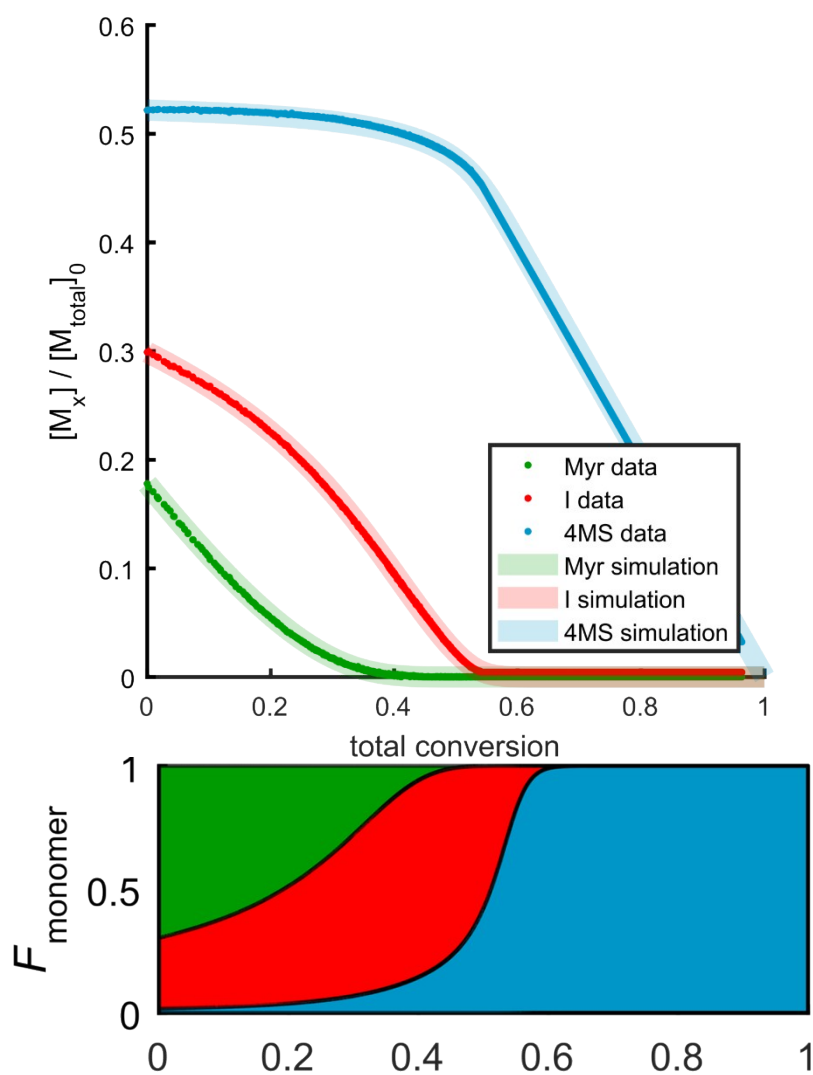


Figure S7 Terpolymerisation experiment and simulation with ideal copolymerisation model for the terpolymerisation of Myr/I/4MS.

As is evident, the simulation in **Figure S7** describes the terpolymerisation adequately. Note that for the simulation only the values for A_0 , B_0 and C_0 as two reactivity ratios are required. An analogous simulation with $A_0 = B_0 = C_0$ was performed to create **Figure 4** and **Figure 5** in the main manuscript.

In-situ ^1H NMR Kinetics

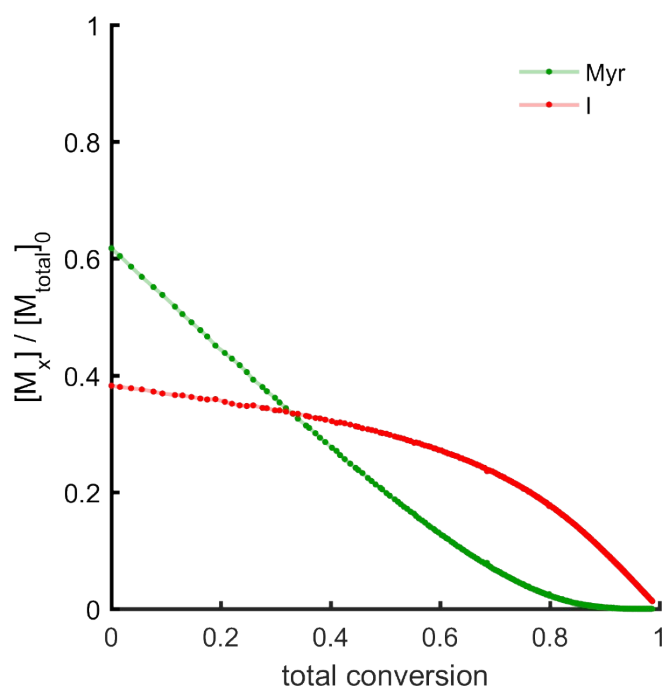


Figure S8 Monomer conversion for the copolymerisation of Myr/I, determined from in-situ ^1H NMR spectroscopy.

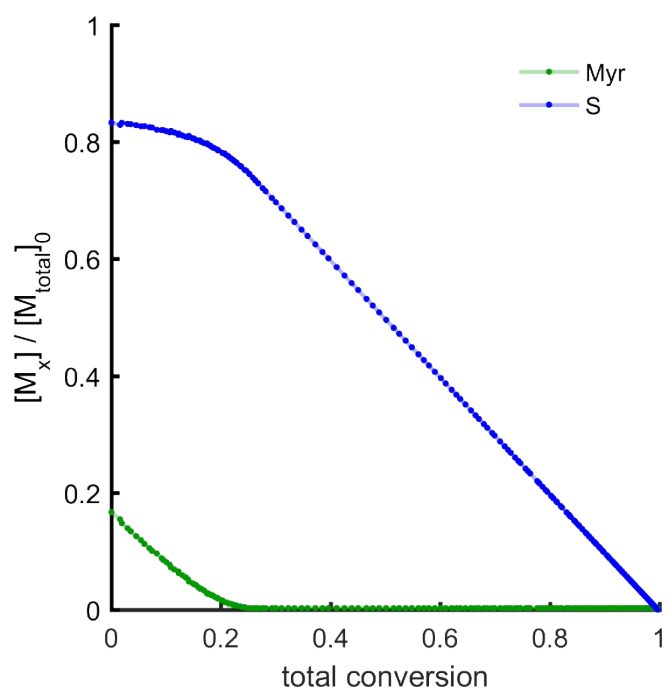


Figure S9 Monomer conversion of the copolymerisation of the Myr/S system.

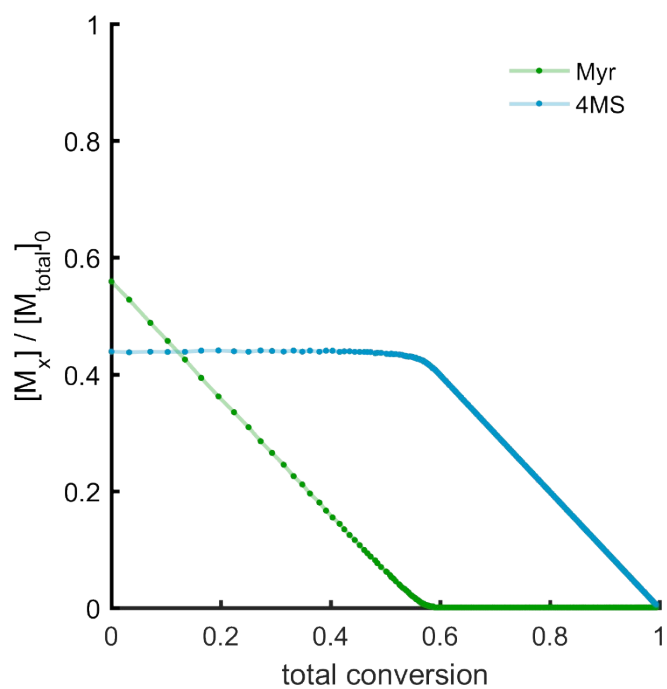


Figure S 10 Monomer conversion for the copolymerisation of the Myr/4MS system.

SEC

SEC (eluent: THF, calibration: PS, detector: UV)

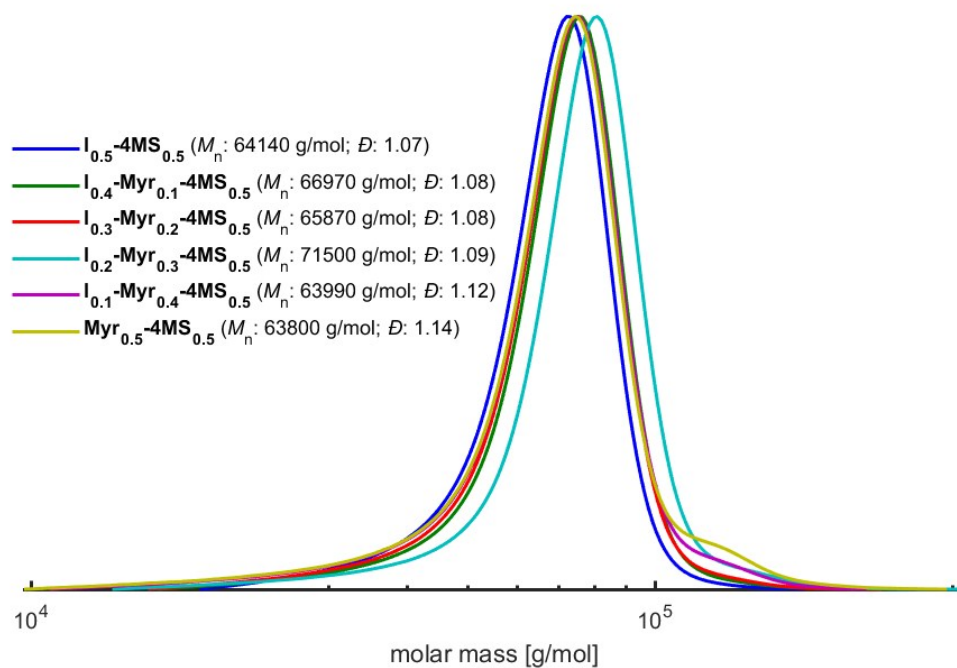


Figure S11 SEC elugrams of 4MS copolymers (Table S2 Entry 1 - 6).

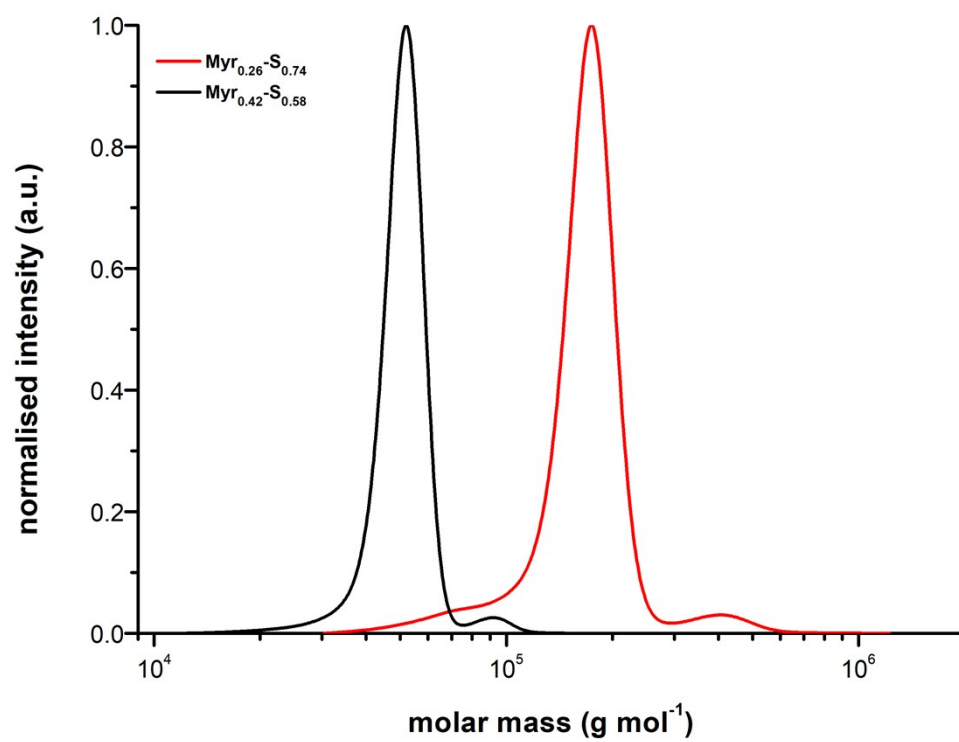


Figure S12 SEC elugrams of styrene (S) copolymers (**Table S2 Entries 7 and 8**).

DSC

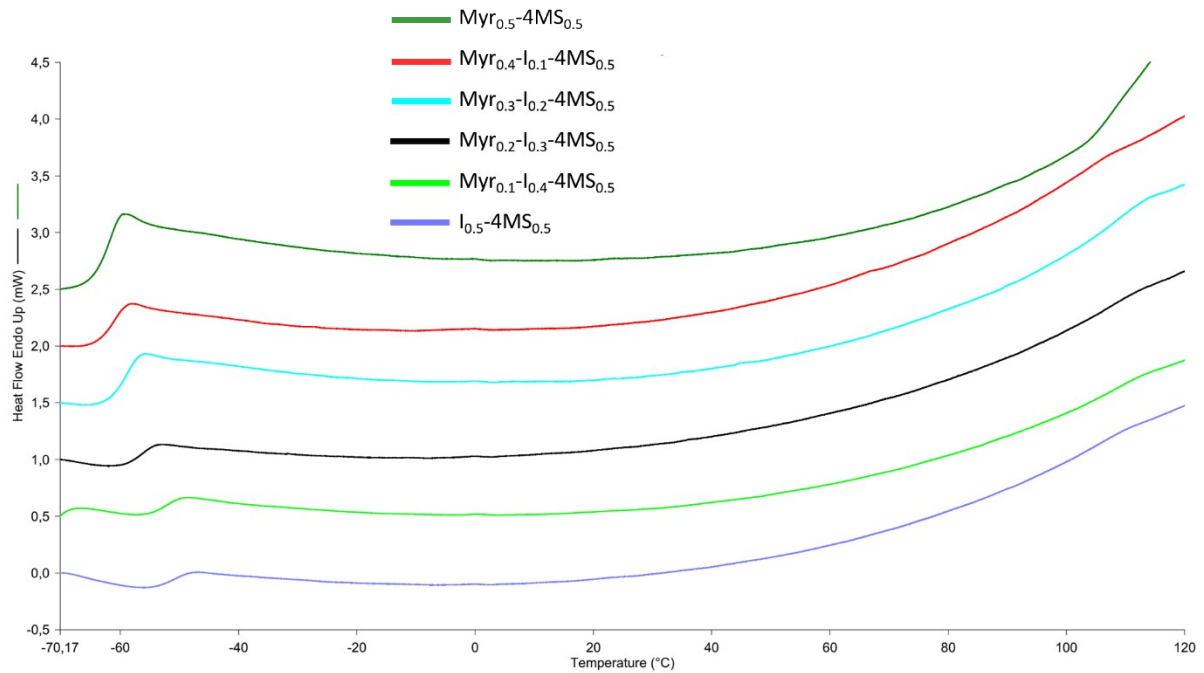


Figure S13 DSC thermograms of 4MS copolymers (Table S2 Entry 1 - 6), heating rate 10 K/min.

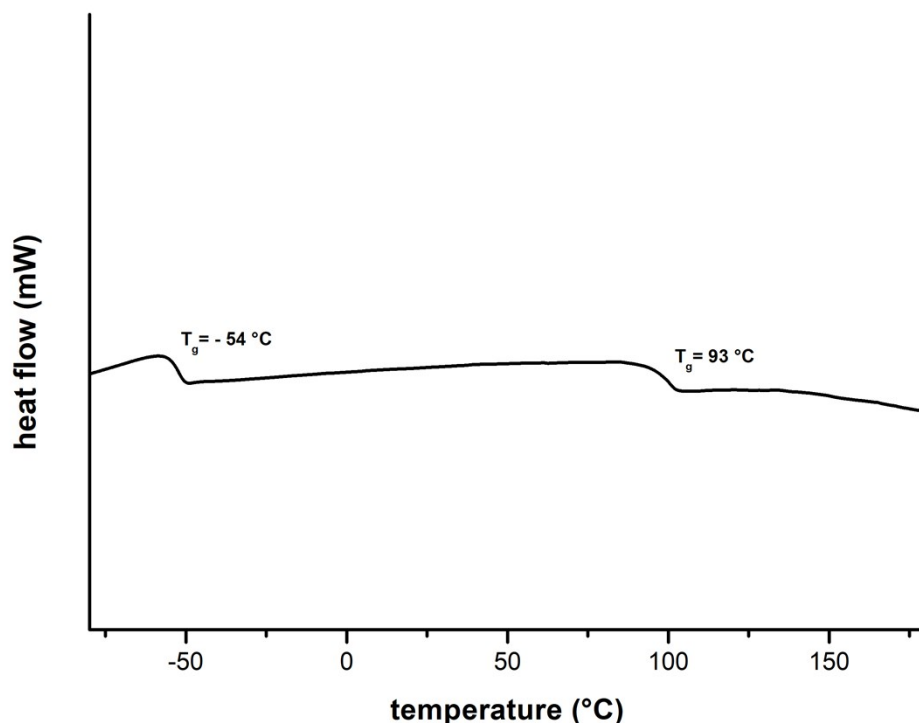


Figure S14 DSC thermogram of Myr_{0.42}-S_{0.58} (Table S2 Entry 7), heating rate 10 K/min.

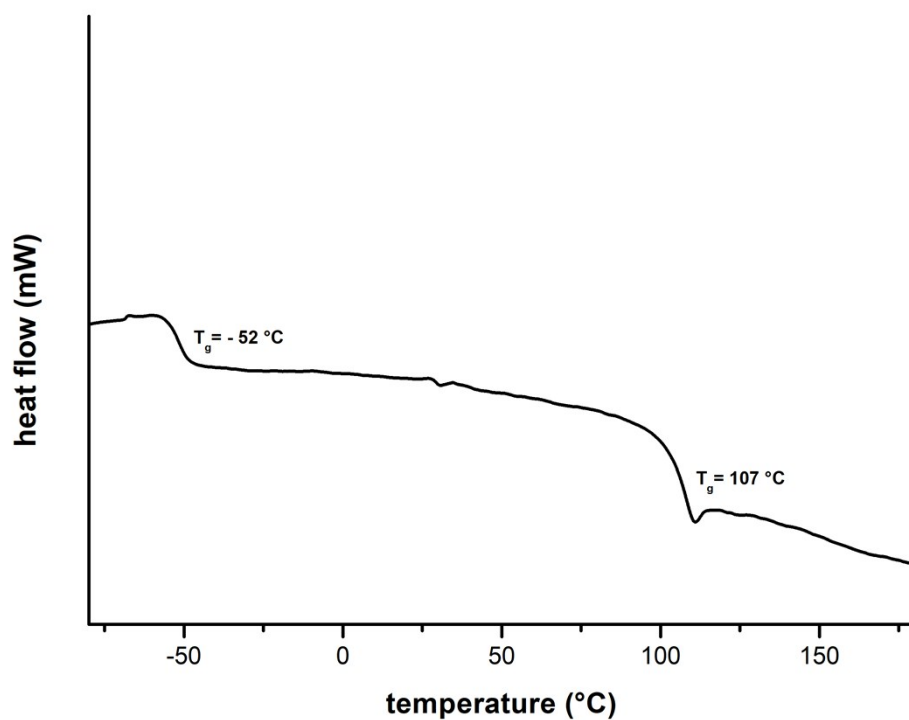


Figure S15 DSC thermogram of Myr_{0.26}-S_{0.74} (Table S2 Entry 8), heating rate 10 K/min.

TEM (transmission electron microscopy)

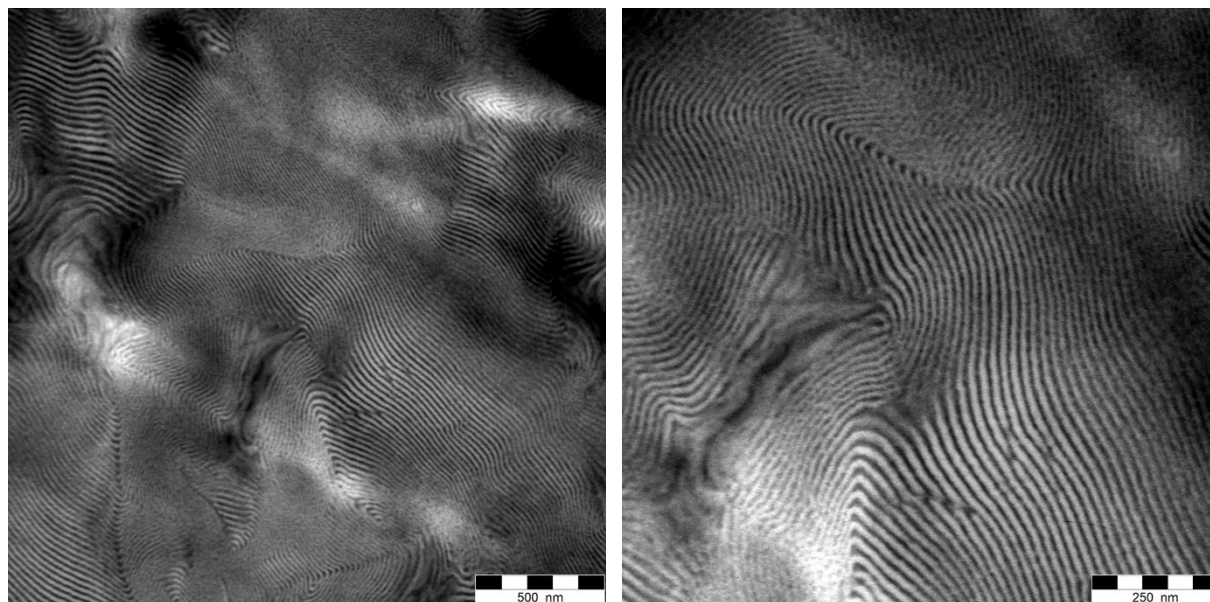


Figure S16 TEM image of I_{0.5}-4MS_{0.5} (Table S2 Entry 1).

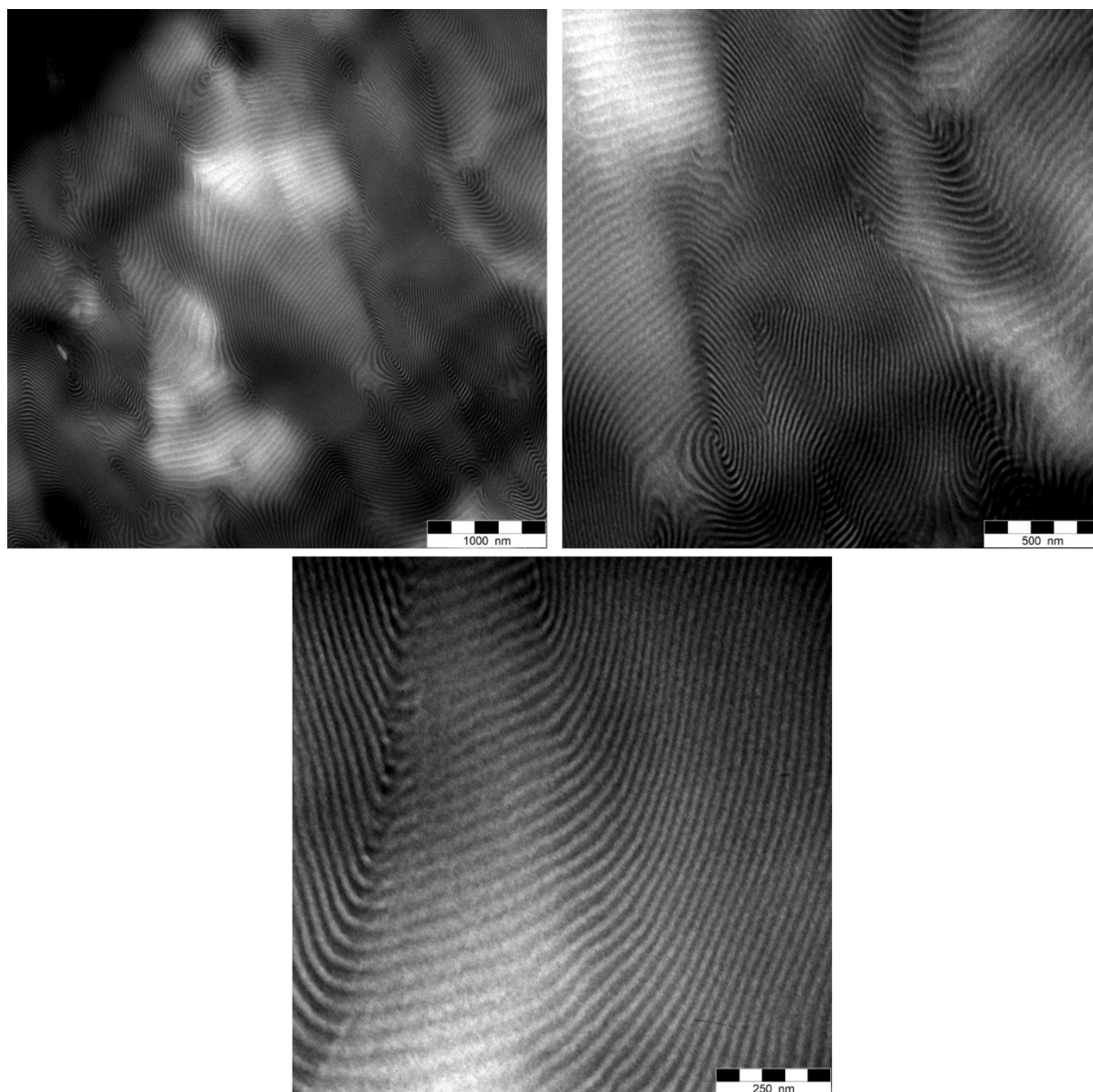


Figure S17 TEM image of Myr_{0.3}-I_{0.2}-4MS_{0.5} (Table S2 Entry 4).

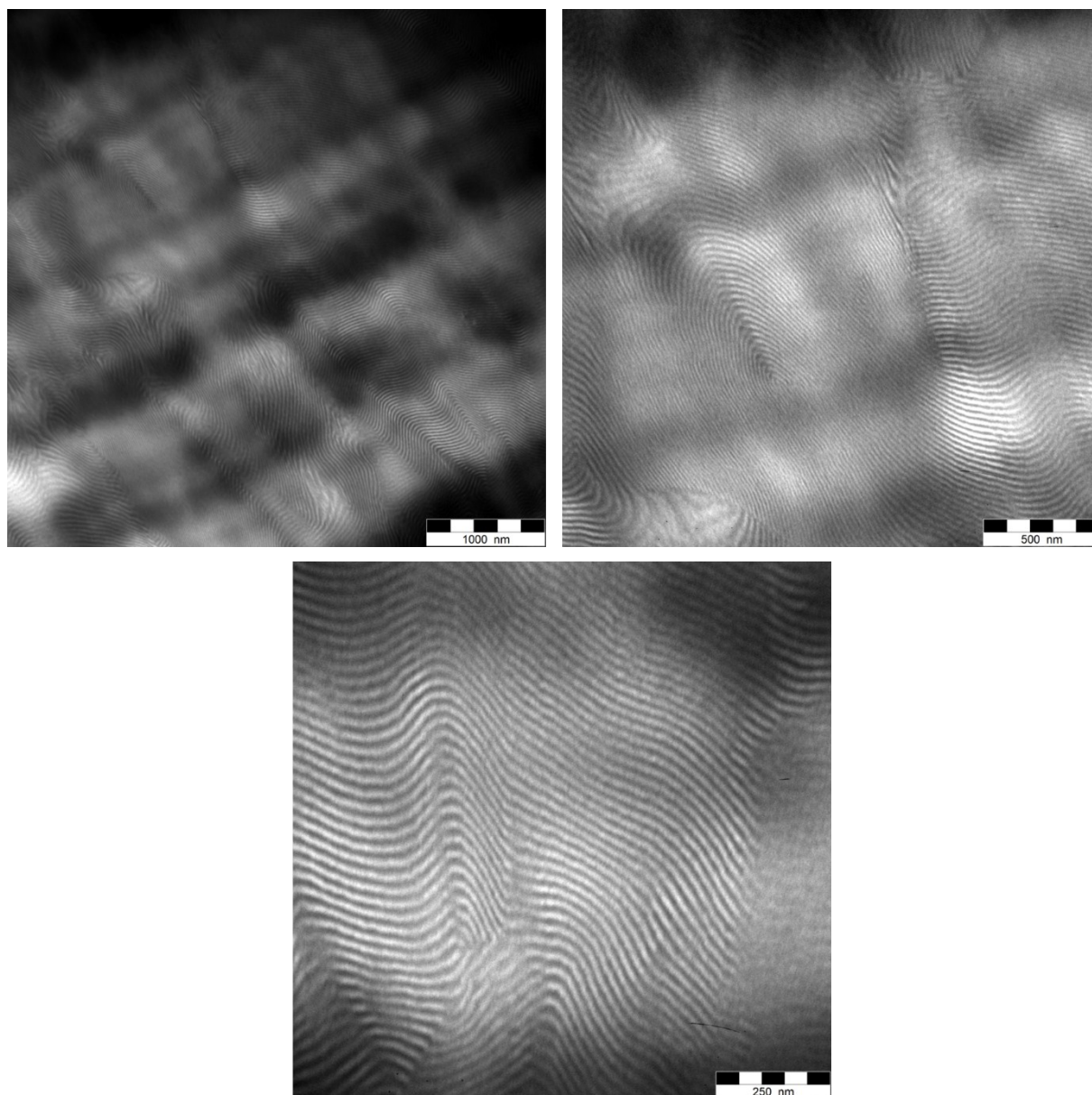


Figure S18 TEM image of Myr_{0.5}-4MS_{0.5} (Table S2 Entry 6).

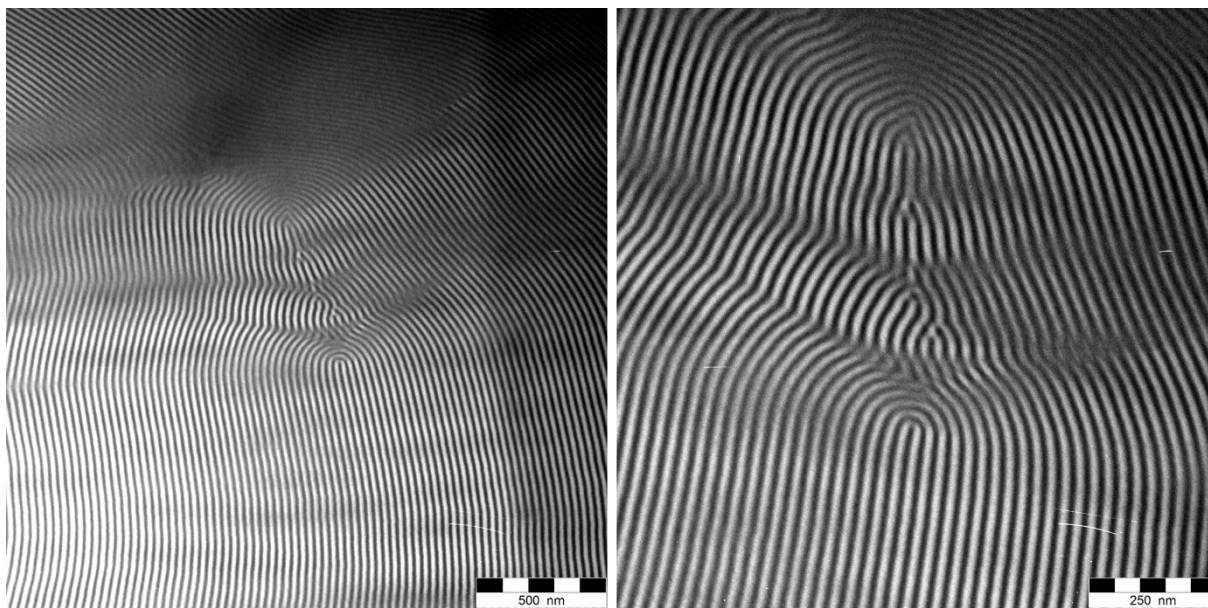


Figure S19 TEM image of Myr_{0.42}-S_{0.58} (Table S2 Entry 7).

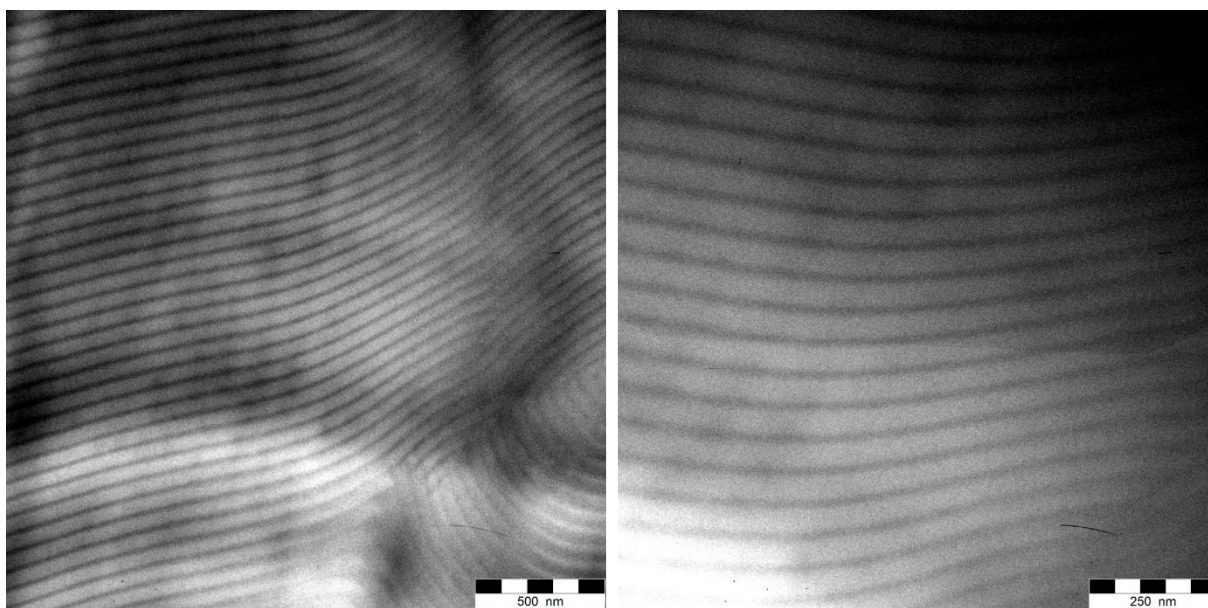


Figure S20 TEM image of Myr_{0.26}-S_{0.74} (Table S2 Entry 8).

SAXS (Small Angle X-ray Scattering)

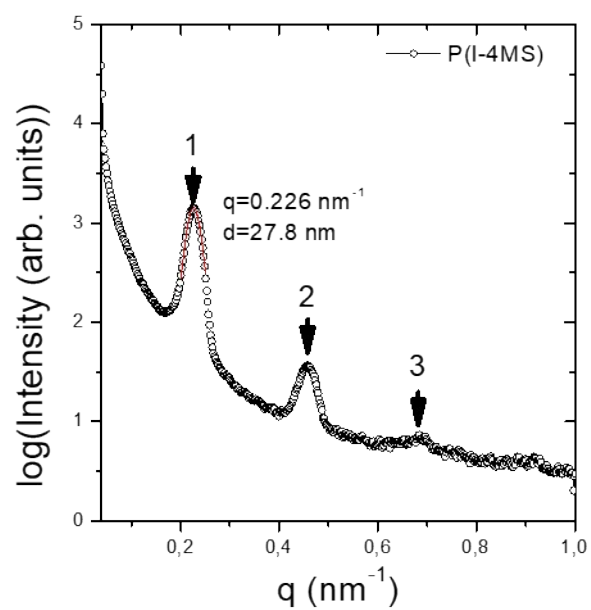


Figure S21 SAXS measurements of $l_{0.5}$ -4MS $_{0.5}$ (Table S2 Entry 1).

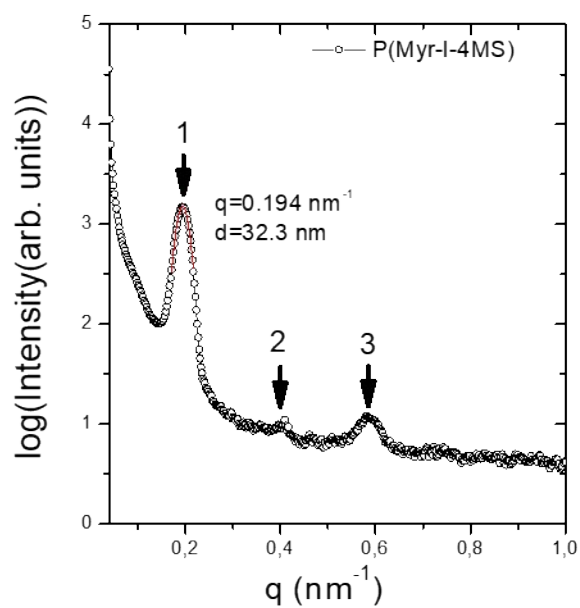


Figure S22 SAXS measurement of $\text{Myr}_{0.3}$ - $l_{0.2}$ -4MS $_{0.5}$ (Table S2 Entry 4).

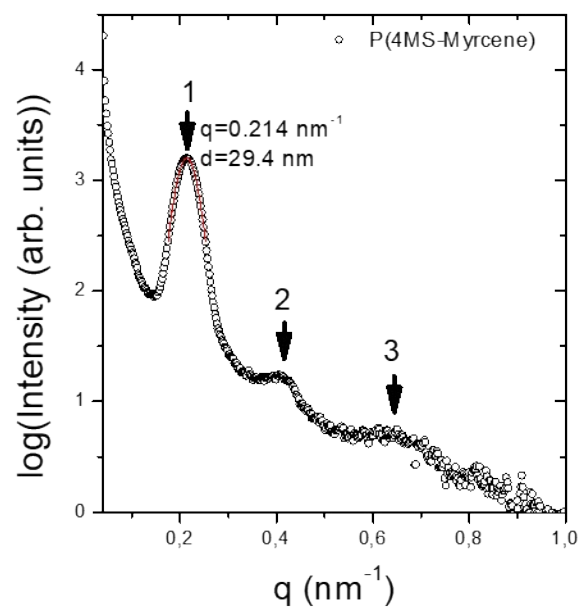


Figure S23 SAXS measurement of Myr_{0.5}-4MS_{0.5} (Table S2 Entry 6).

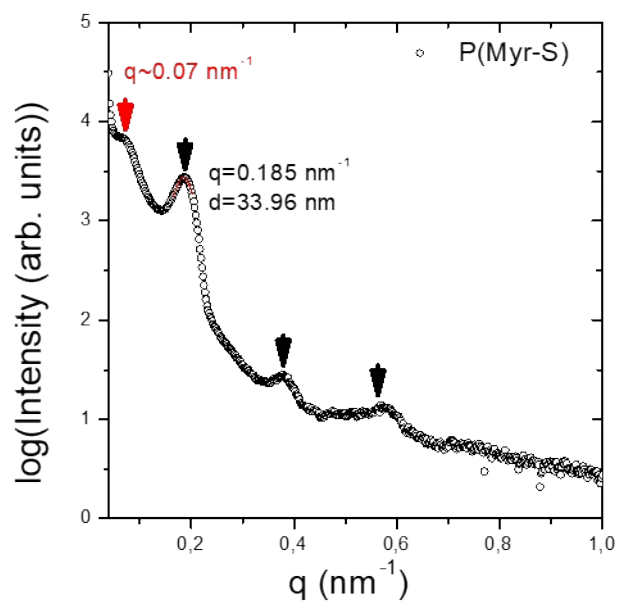


Figure S24 SAXS measurement of Myr_{0.42}-S_{0.58} (Table S2 Entry 7).

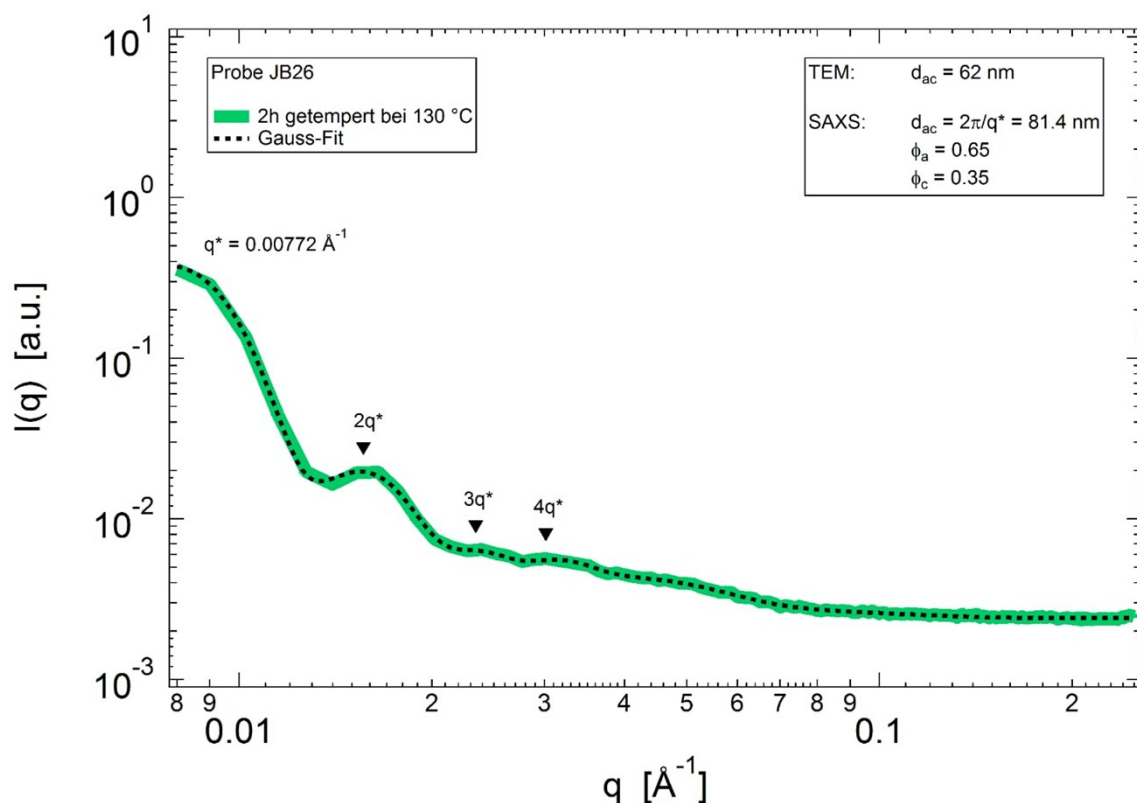


Figure S25 SAXS measurement of Myr_{0.26}-S_{0.74} (**Table S2 Entry 9**).

References

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