

Trans-stereospecific polymerization of butadiene and random copolymerization with styrene using borohydrido rare earths / magnesium dialkyl catalysts

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– SUPPLEMENTARY DATA –

Figure S1. ¹H NMR spectrum (300 MHz) of polybutadiene sample as synthesized in run 9. Details of peak attribution for ¹³C NMR spectra of polybutadiene.

MALDI – ToF analysis of butadiene-styrene random copolymer.

Figure S2: MALDI-ToF spectrum for butadiene-styrene copolymer isolated as described in the experimental section, rough data.

Figure S3: spectrum enlargement (black line) and comparison to the simulation (red dots) with $s = 0$ and $b = 12$.

Figure S4: discrimination between $[s; b]$ and $[s-1; b+2]$ neighboring peaks (4 g/mol shift).

Figure S5. Intensity fit between rough data and simulated distributions having the Poisson statistics.

Figure S6: Full spectra of simulated distributions having the Poisson statistics that fit with intensities of rough data peaks.

Figure S7: Distribution of butadiene-styrene copolymers as determined by MALDI-ToF analysis

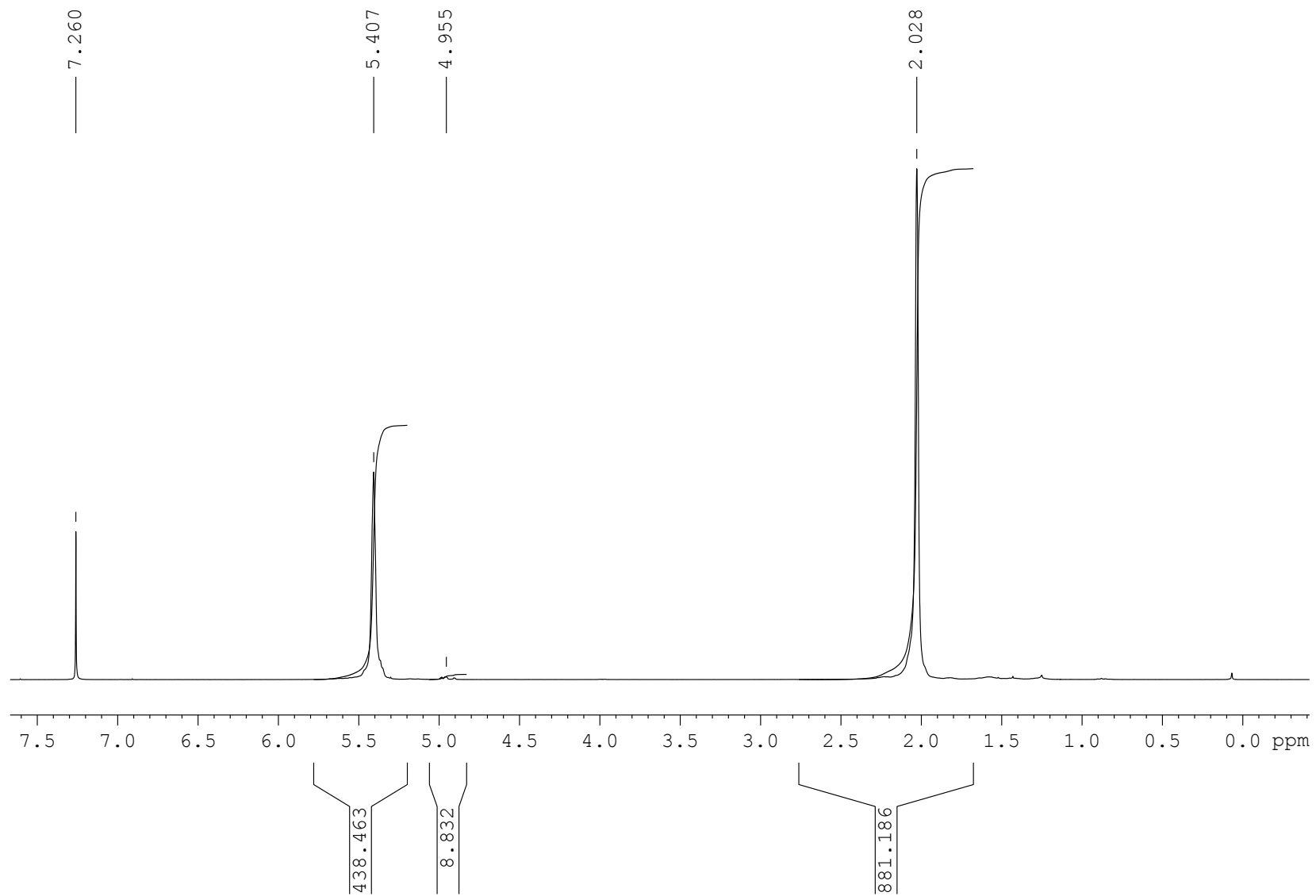


Figure S1. ¹H NMR spectrum (300 MHz) of polybutadiene sample as synthesized in run 9. (CDCl₃)

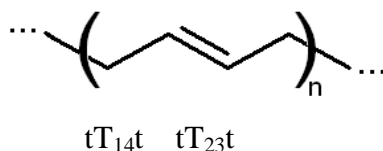
Details of peak attribution for ^{13}C NMR spectra of polybutadiene.

Naming convention: in accordance with Makhiyanov [ref], each unit in the polymeric chains is denoted by an uppercase letter. Two lowercase letters describe the neighboring units. The left one refers to the preceding unit, which was bonded to the polymeric chain before the unit under study, in direction of the initiator. The right one refers to the next one, bonded after and towards the end of chain. The subscript number refers to the carbon number, the first one being linked to the preceding unit.

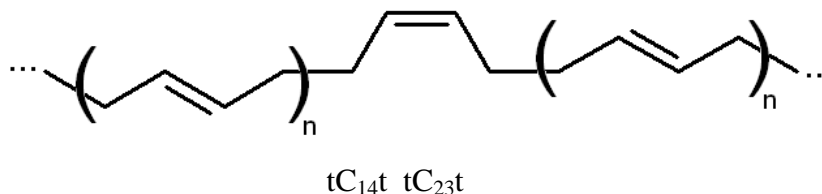
T: *trans*-1,4-insertion of butadiene
 C: *cis*-1,4-insertion of butadiene
 V: vinyl by 1,2 insertion of butadiene
 B: butyl initiator
 E: ethyl initiator
 D: ethylidene *i.e.* $=\text{CH}-\text{CH}_3$ end-group
 A: allyl *i.e.* $-\text{CH}_2-\text{CH}=\text{CH}_2$ end-group

Example: $\text{vT}_{1\text{c}}$ is the 1st carbon of a *trans* unit, inserted after a vinyl and followed by a *cis* unit.

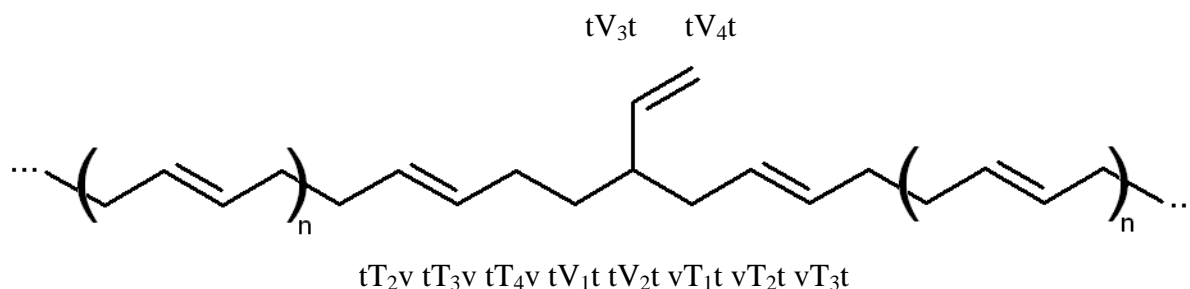
Regular *trans* sequence:



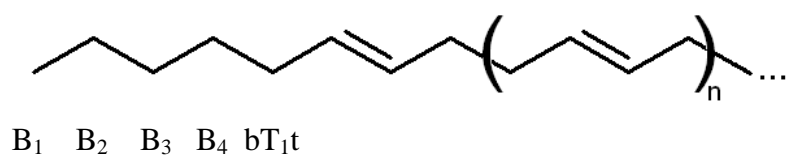
Cis defect in *trans* chain:



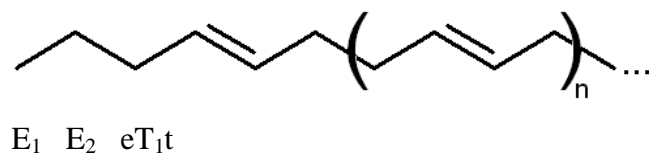
Vinyl unit or -1,2- defect in a *trans* chain:



Chain tip formed by butyl initiator:

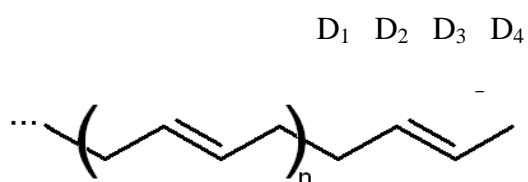


Chain tip formed by ethyl initiator:

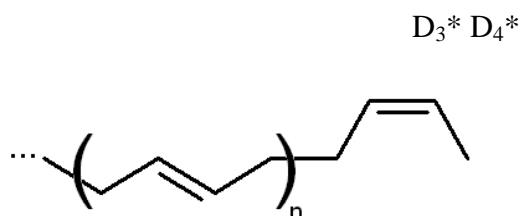


Chain end formed by hydrolysis at the 4th carbon

trans-ethylidene:

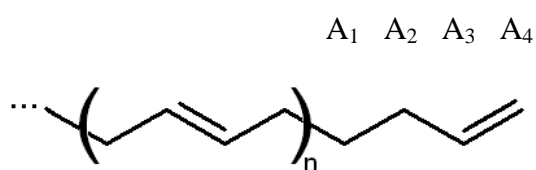


cis-ethylidene:



Chain end formed by hydrolysis at the carbon number 2

Allyl-shaped end:



MALDI – ToF analysis of butadiene-styrene copolymers.

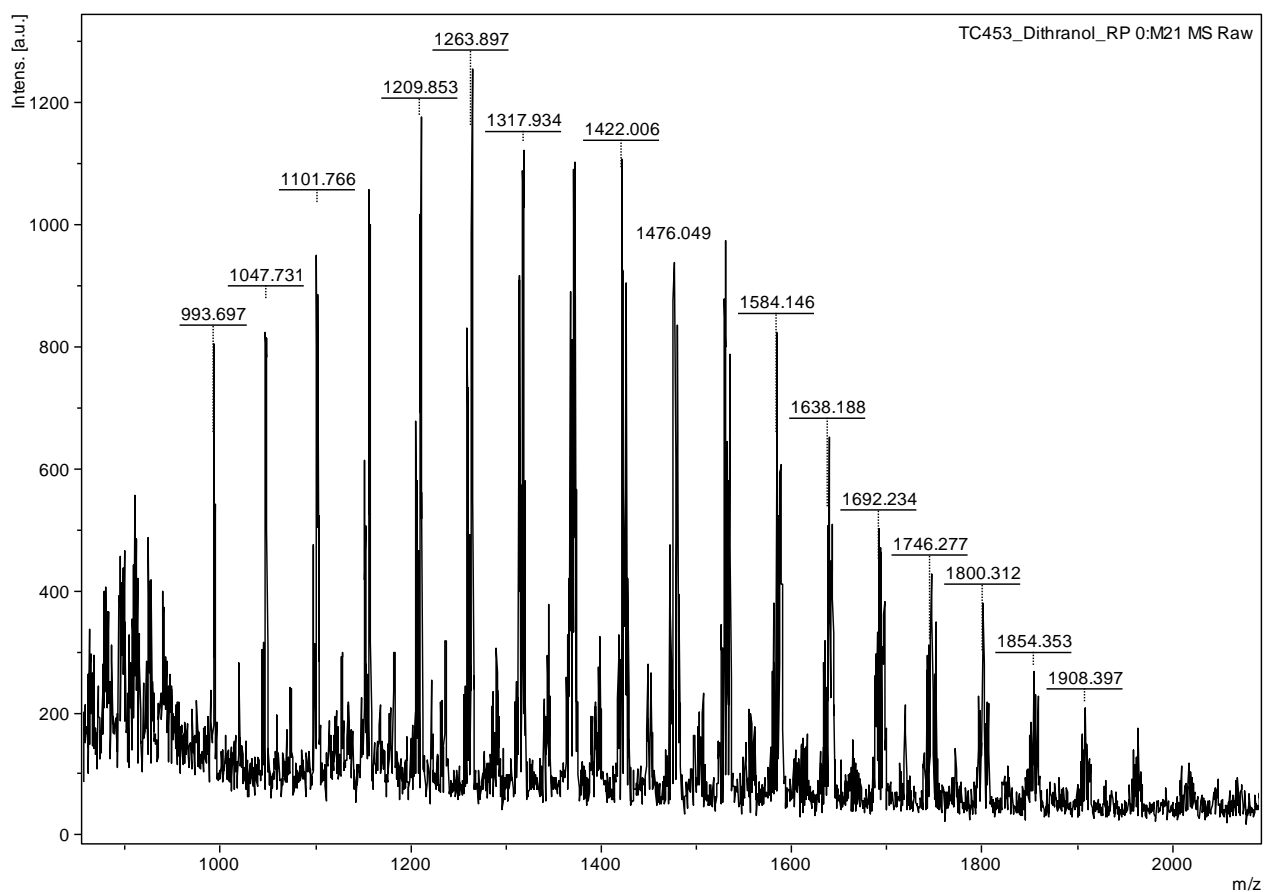
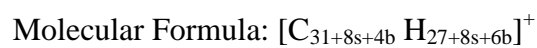
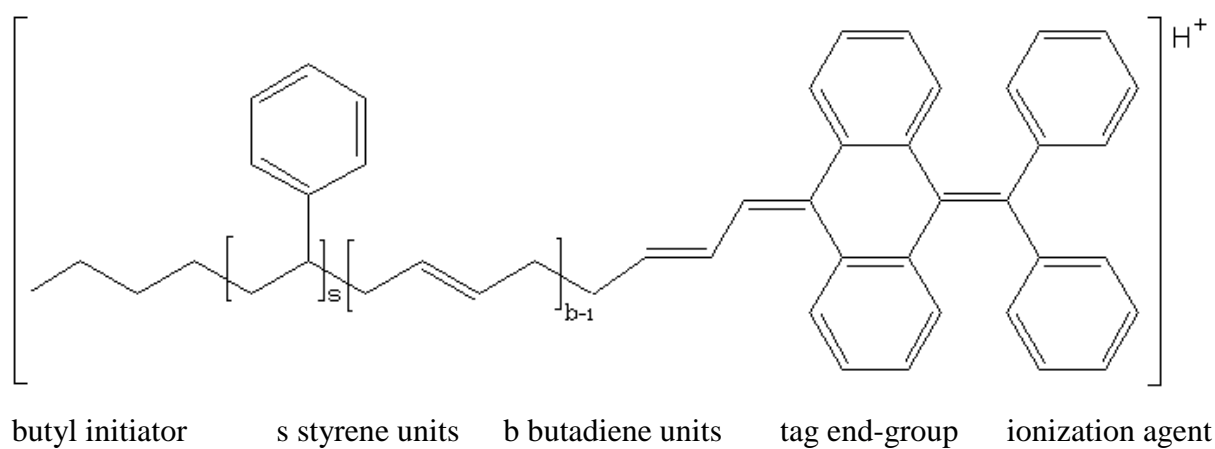


Figure S2: MALDI-ToF spectrum for butadiene-styrene copolymer isolated as described in the experimental section, rough data.

Model compounds used for simulated spectra:



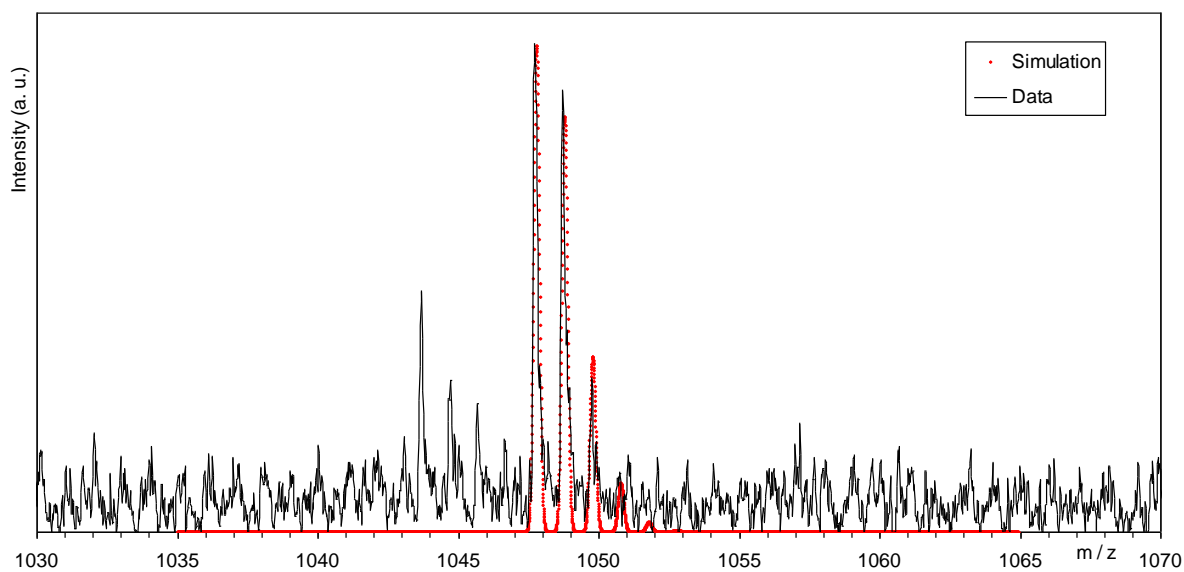


Figure S3: spectrum enlargement (black line) and comparison to the simulation (red dots) with $s = 0$ and $b = 12$.

Coordinates of the above spectrum peaks, compared to molar masses and relative abundances of molecular formulas $^{12}\text{C}_{(79-i)}\text{C}_i\text{H}_{99}$:

m/z [rel. intens.]	1 st peak (i = 0)	2 nd peak (i = 1)	3 rd peak (i = 2)	4 th peak (i = 3)
Observed	1047.709 [100]	1048.715 [90]	1049.742 [32]	1050.749 [12]
Calculated	1047.775 [100]	1048.778 [85]	1049.781 [36]	1050.785 [10]

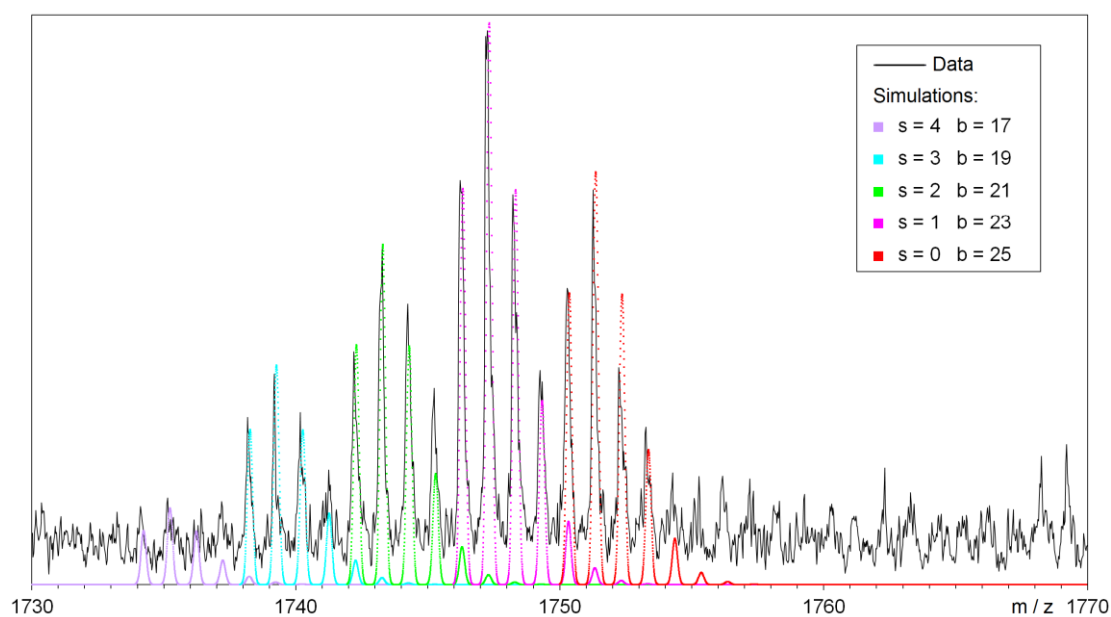


Figure S4: discrimination between $[s; b]$ and $[s-1; b+2]$ neighboring peaks (4 g/mol shift).

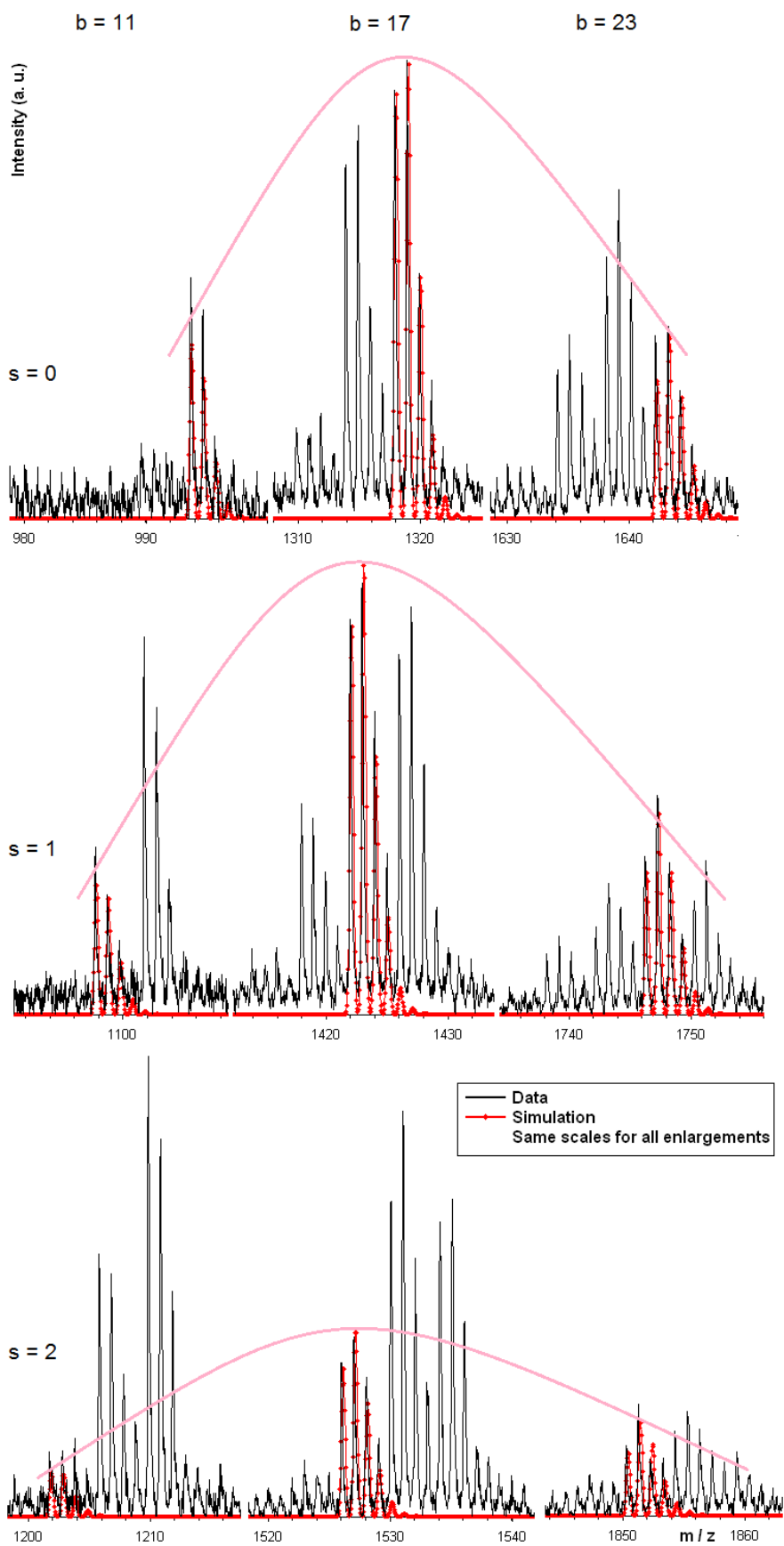


Figure S5. Intensity fit between rough data and simulated distributions having the Poisson statistics. Enlarged areas for selected numbers of styrene and butadiene, as representative examples.

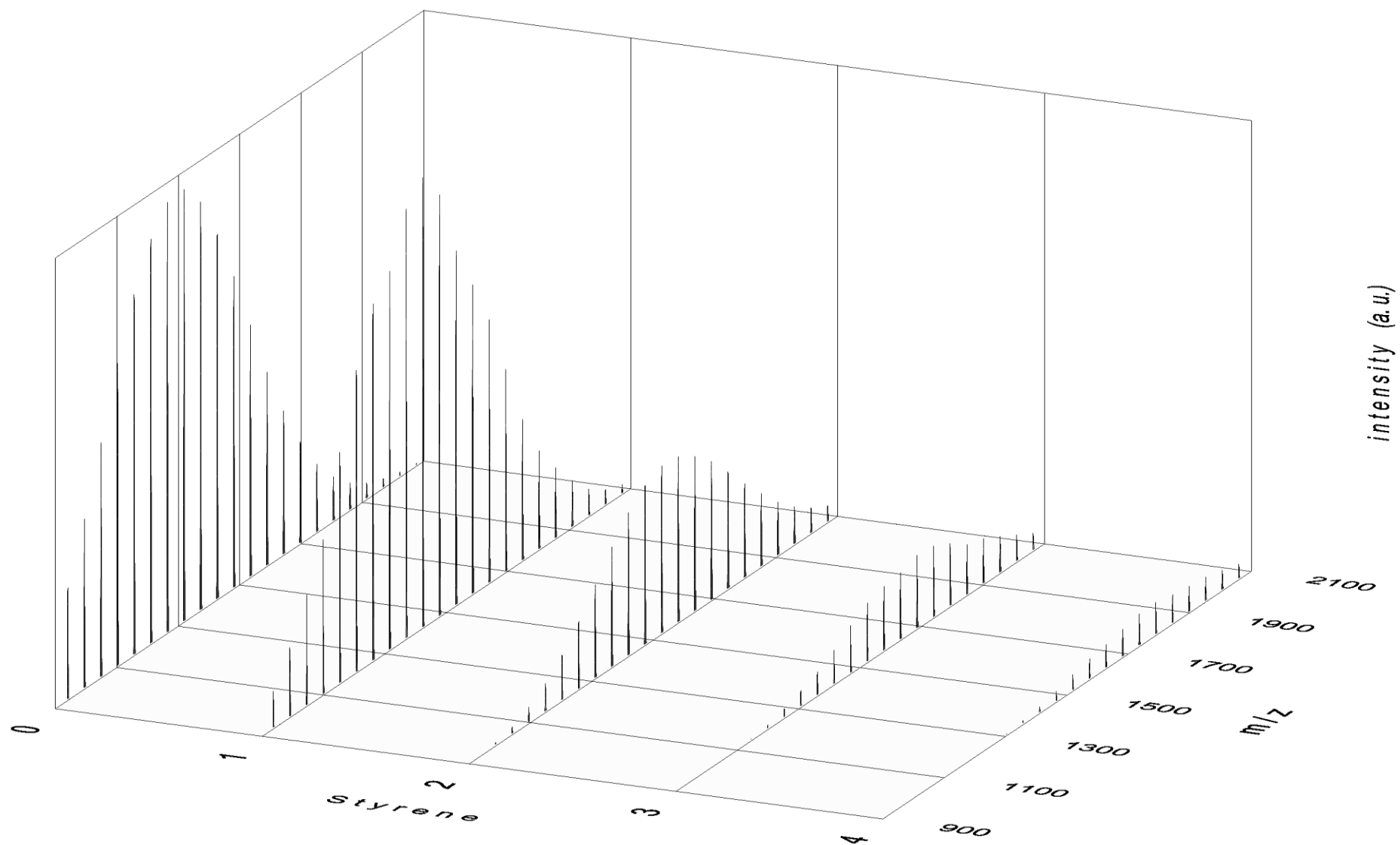


Figure S6: Full spectra of simulated distributions having the Poisson statistics that fit with intensities of rough data peaks.

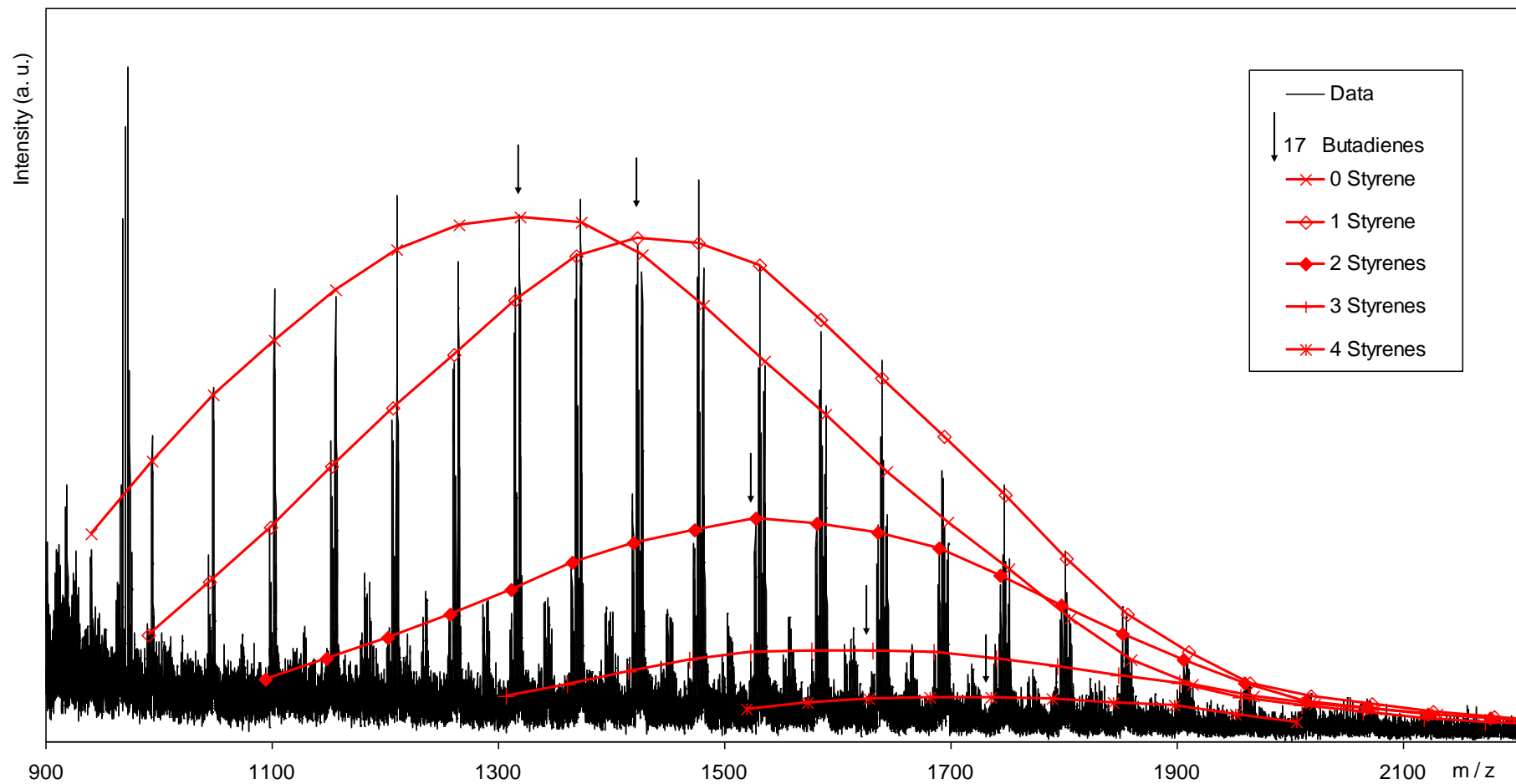


Figure S7: Distribution of butadiene-styrene copolymers as determined by MALDI-ToF analysis