Quantification of Molecular Weight Discrimination in Grafting to Reactions from Ultrathin Polymer Films by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry.

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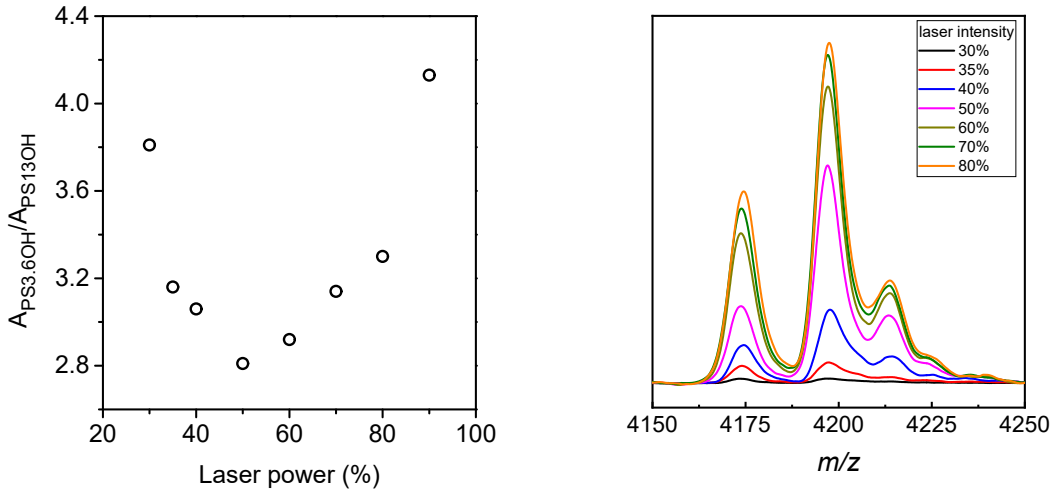

Figure SI1. $PS_{3.6}OH$ and $PS_{13}OH$ areas ratio as a function of the laser power.

Figure SI1. MALDI-TOF MS spectra recorded for the $PS_{3.6}OH$ and $PS_{13}OH$ in B0.50 mixture at different laser power percentage.

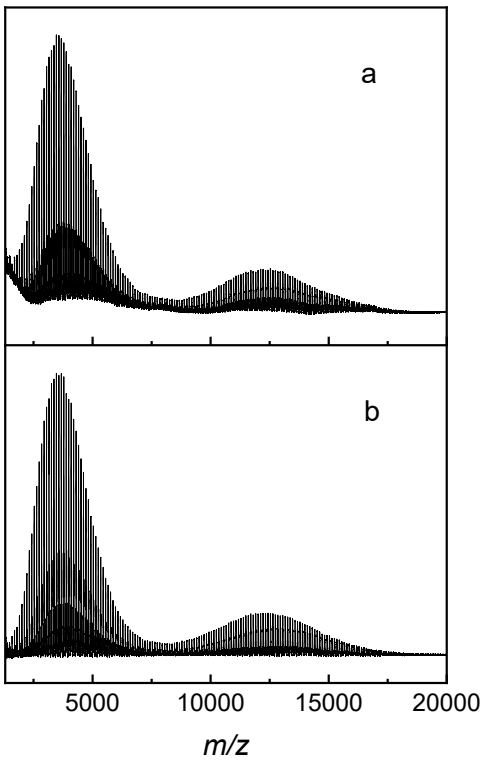

Figure SI2 MALDI-TOF MS spectra recorded for the $PS_{3.6}OH$ and $PS_{13}OH$ in B0.50 mixture without (a) and with (b) baseline correction.

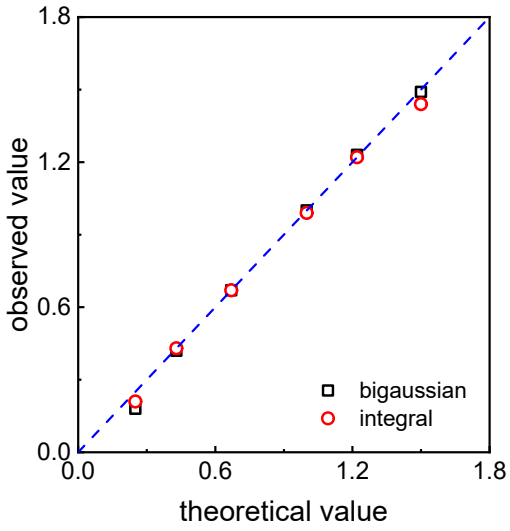

Figure SI3. Observed vs Thoretical values

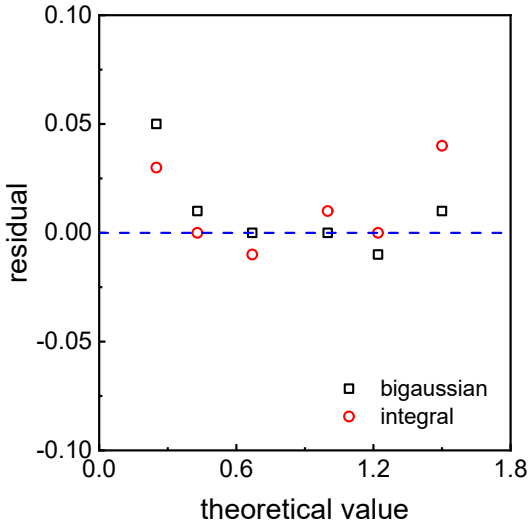

Figure SI4. Residual vs Thoretical values

Tab SI 1. Observed and residual values obtained both with bigaussian and integral data treatment.

Sample	Theoretical value	Bigaussian		Integral	
		Observed values	Residual	Predicted values	Residual
B0.60	1.50	1.49	0.01	1.44	0.04
B0.55	1.22	1.23	-0.01	1.22	0.00
B0.50	1.00	1.00	0.00	0.99	0.01
B0.40	0.67	0.67	0.00	0.67	-0.01
B0.30	0.43	0.42	0.01	0.43	0.00
B0.20	0.25	0.18	0.05	0.21	0.03

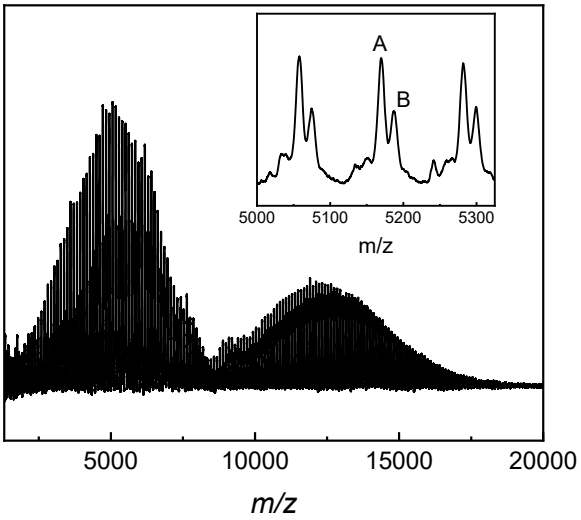

Figure SI5. MALDI-TOF MS spectra of Bd0.41 blend of $PS_{d5.2}OH$ and $PS_{13}OH$. In the inset, expanded range (m/z 4000-4400 and 11000-11400) where A and B refers to the structures already illustrated in Figure 1 for hydrogenated or deuterated polystyrene.

Molar ratio of the grafted chains calculated from MALDI analysis. The numbers of $PS_{3.6}OH$ and $PS_{13}OH$ chains contained in the spin-coated layer (per unit area 1 nm x 1nm) are defined as $\Sigma_{PS3.6OH}$ and Σ_{PS13OH} respectively and calculated using the Equations S1 and S2.

$$\Sigma_{PS3.6OH} = \frac{Hd\,N_A}{M_n(PS_{3.6}OH) + \frac{mol_{PS13OH}}{mol_{PS3.6OH}} M_n(PS_{13}OH)} \quad \text{Eq. S1}$$

$$\Sigma_{PS13OH} = \frac{Hd\,N_A}{\frac{mol_{PS3.6OH}}{mol_{PS13OH}} M_n(PS_{3.6}OH) + M_n(PS_{13}OH)} \quad \text{Eq. S2}$$

H defines the thickness of the spin-coated layer (nm), d is the polystyrene density (1.05 g/cm^3), N_A is the Avogadro's number, M_n ($PS_{3.6}OH$) and M_n ($PS_{13}OH$) are respectively the number average molecular weights of the $PS_{3.6}OH$ and the $PS_{13}OH$ samples (i.e. 3600 and 13000 g/mol).
The ratio between the mole number of the $PS_{3.6}OH$ and the $PS_{13}OH$ in the spin-coated samples was obtained from the MALDI analysis on the S1, S2 and S3 samples (Table 2).

The same calculations can be carried out on the unreacted parts of the samples (G300 and G2100), replacing H with (H-h), where h is the thickness of the grafted brush, and the ratio $mol_{PS3.6OH}$ / mol_{PS13OH} with the experimental one obtained from the MALDI analysis of the unreacted chains (Table 2). The values of $\Sigma_{PS3.6OH}$ and Σ_{PS13OH} obtained are then the numbers of $PS_{3.6}OH$ and $PS_{13}OH$ contained in the unreacted part of the spin-coated layers after the annealing process.

Subtracting from the $\Sigma_{PS3.6OH}$ and Σ_{PS13OH} values obtained for the starting spin-coated sample the $\Sigma_{PS3.6OH}$ and Σ_{PS13OH} values obtained for the unreacted part, the number of $PS_{3.6}OH$ and $PS_{13}OH$ chains in the grafted brush is obtained. From these numbers the molar ratios reported in the last column of the Table 3 are easily calculated.

Molar ratio of the grafted chains calculated from TGA-GC-MS analysis.
The numbers of $PS_{3.6}OH$ and $PS_{13}OH$ chains grafted on the substrate (per unit area 1 nm x 1nm) are defined as $\Sigma_{PSd5.2OH}$(brush) and Σ_{PS13OH}(brush) respectively and calculated using the Equations S3 and S4.

$$\Sigma_{PSd5.2OH}(brush) = \frac{\frac{A_T Sd}{(A_T Sd + A_T S)} h\,d\,N_A}{M_n(PS_{d5.2}OH)} \quad \text{Eq. S3}$$

$$\Sigma_{PS13OH}(brush) = \frac{\frac{A_T S}{(A_T Sd + A_T S)} h\,d\,N_A}{M_n(PS_{13}OH)} \quad \text{Eq. S4}$$

h defines the thickness of the grafted layer (nm), d is the polystyrene density (1.05 g/cm^3), N_A is the Avogadro's number, M_n ($PS_{d5.2}OH$) and M_n ($PS_{13}OH$) are respectively the number average molecular weights of the $PS_{d5.2}OH$ and the $PS_{13}OH$ samples (i.e. 5.200 and 13000 g/mol).

Determination of the grafting density due to preferential reaction of the lower molar mass species

The grafting density (Σ) in a brush layer is calculated according to the following equation:

$$\Sigma = (H\ N_A\ \rho)/\ M_n$$

where H is the thickness of the brush layer, N_A is the Avogadro's number and ρ is the density of the polymer. Table SI 2 reports the grafting densities assuming that that the molecular weight of the polymeric blend (Mn) in the brush layer is perfectly equivalent to the one of the as prepared blends (theoretical Mn) and Mn determined by MALDI TOF analysis (MALDI TOF Mn).

Tab SI 2. Grafting density values

Sample	**Time (s)**	**Grafting density using Theoretical Mn (chains/nm^2)**	**Grafting density using MALDI-TOF Mn (chains/nm^2)**
B0.50	300	0.30	0.29
	2100	0.37	0.42
Bd0.41	300	0.34	0.35
	2100	0.37	0.41