

Supporting Info

Inside the Brush: Partition by Molecular Weight in Grafting to Reactions from Melt

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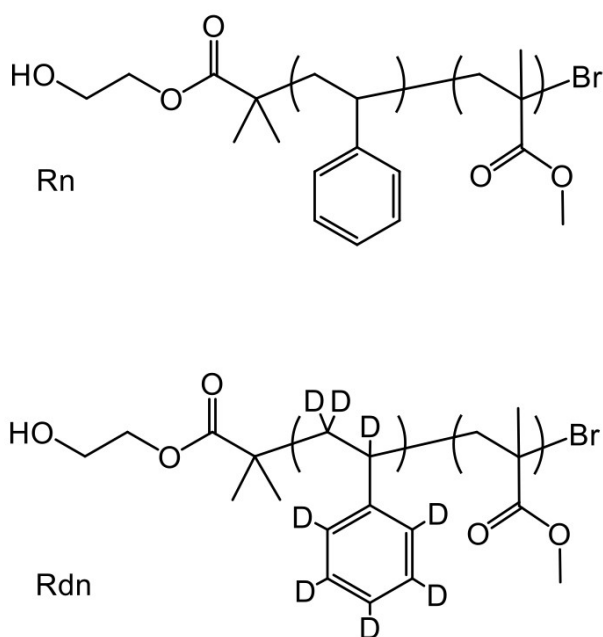


Figure 1S. Structures of the hydroxy terminated poly(styrene-*r*-methyl methacrylate) (Rn) and partly deuterated hydroxy terminated poly(styrene d₈-*r*-methyl methacrylate) random copolymers (Rdn).

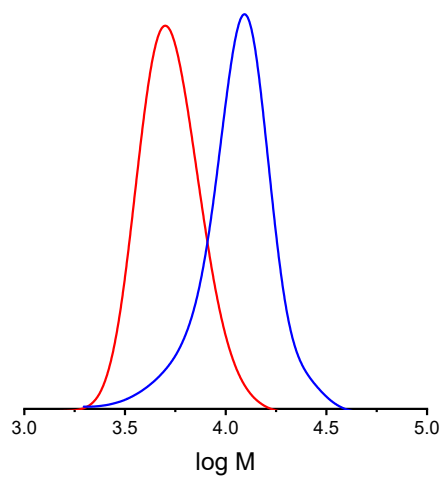


Figure 2S. SEC Curves of samples R5.4 (blue) and Rd11.2 (red).

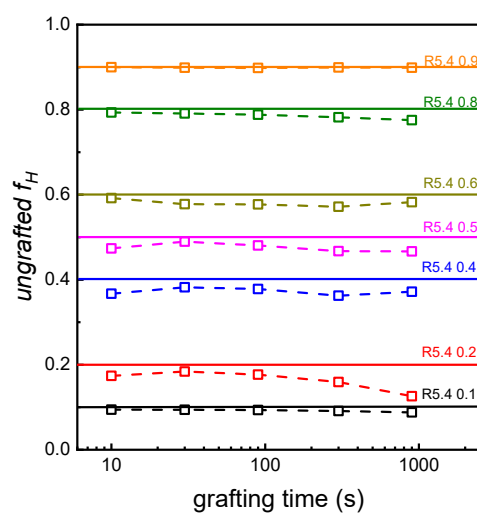


Figure 3S. Molar fraction f_H of R5.4 in the layer of unreacted chains during the grafting process of all the blends as a function of time. The continuous lines indicates the starting compositions of the various blends.

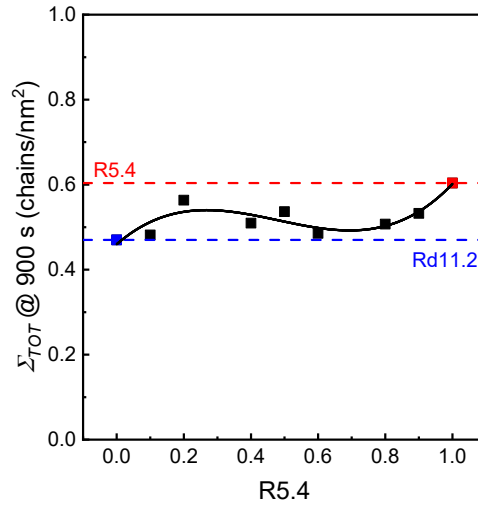


Figure 4S. Total grafting density of the brush layer for different blends reported as a function of the molar fraction of R5.4 after 900 s grafting time for blends grafted at 250°C.

Grafting densities calculation.

The molar fraction of deuterated styrene on the total styrene amount in a grafted brush is named f and is obtained using the Equation S1.

$$f = \frac{1.05 A_{STY-d8}}{1.05 A_{STY-d8} + A_{STY}} \quad (S1)$$

A_{STY-d8} and A_{STY} are the chromatographic peak integrals relative to deuterated and hydrogenated styrene respectively, obtained by TGA-GC-MS analysis. The values of A_{STY-d8} and A_{STY} are proportional to the number of deuterated and hydrogenated monomers generated and detected during the analysis. The factor of 1.05 is a numerical correction to account for the different mass response factor of the monomers.

The grafting densities of deuterated and hydrogenated chains, indicated respectively as Σ_D and Σ_H , are calculated using Equation S2 and S3.

$$\Sigma_D = \frac{f H d N_A}{M_n^D} \quad (S2)$$

$$\Sigma_H = \frac{(1 - f) H d N_A}{M_n^H} \quad (S3)$$

In the equations, H is the thickness of the grafted brush, f is the deuterated styrene fraction defined in Eq. S1, d is the density of the random copolymer brush and M_n^D (M_n^H) is the number average molecular weight of the deuterated (hydrogenated) polymer.

The total grafting density (Σ_{Tot}) is simply the sum of Σ_D and Σ_H .