Electronic Supplementary Material (ESI) for Polymer Chemistry.

Short vs long chains competition during "*grafting to*" process from melt

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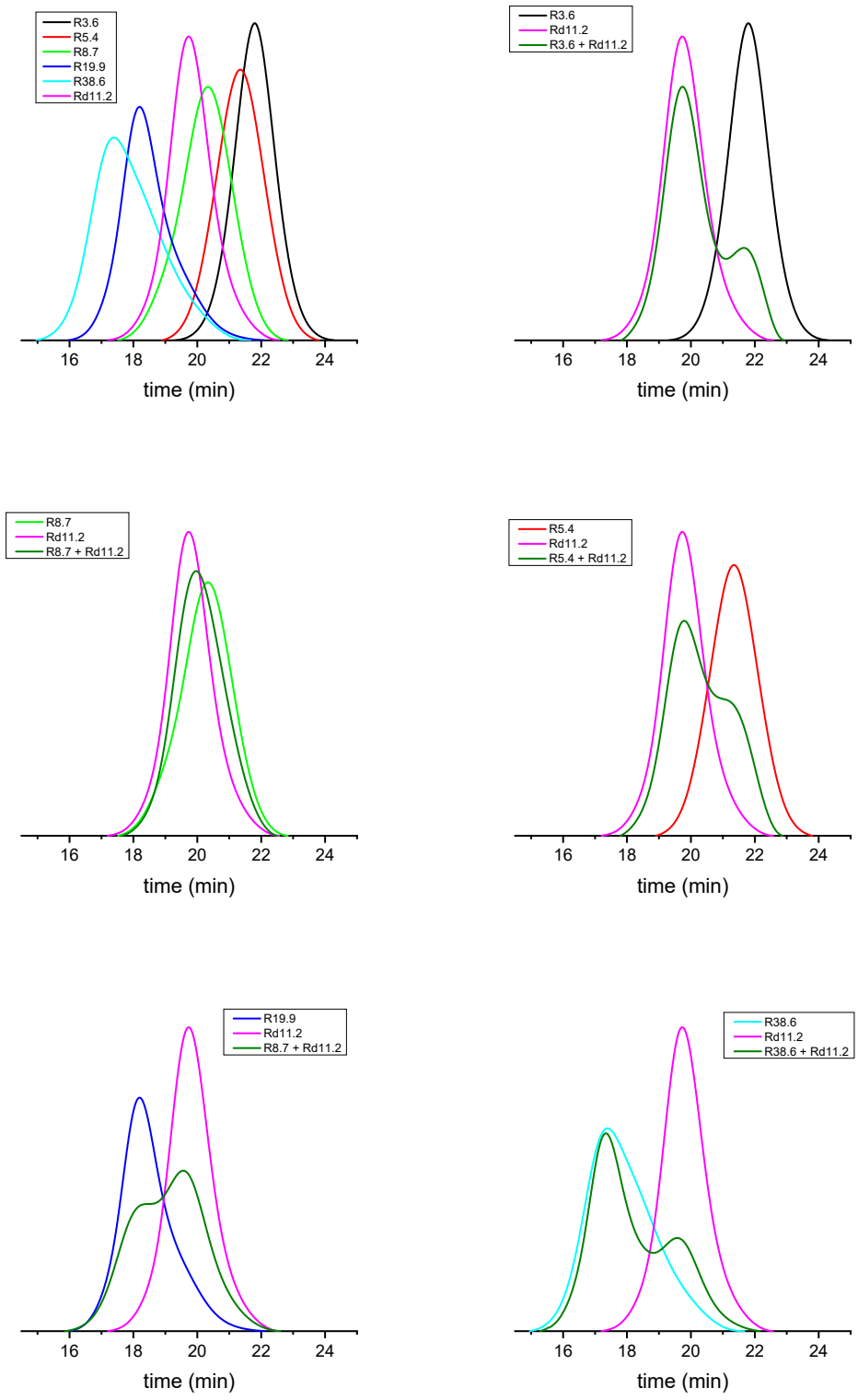

Fig. 1S SEC curves of **Rn** and **Rd11.2** as well as the 1:1 blends.

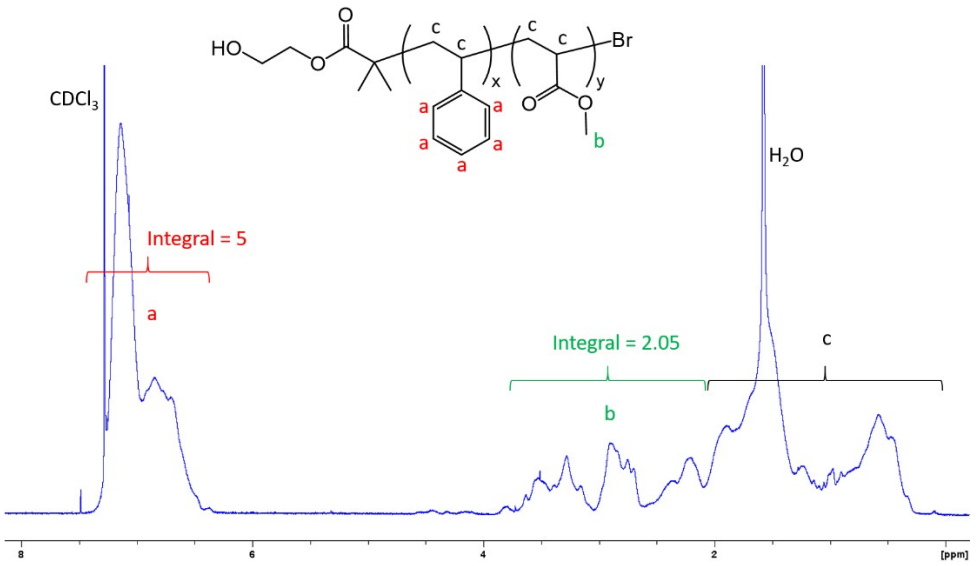

Fig. 2S ^{1}H NMR of sample R5.4. The styrene unit fraction was estimated from the integrals of a and b protons and results S%=59.3. The partial overlapping of signals at 2.1 ppm was resolved by deconvoluting the two peaks.

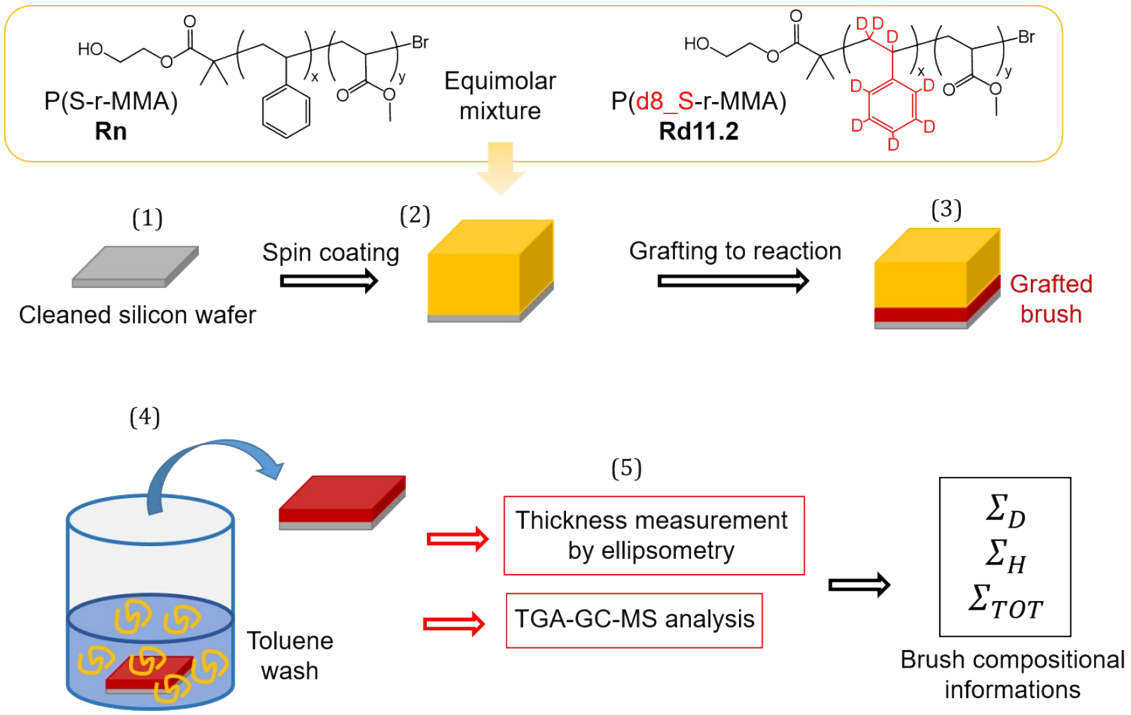

Figure 3S Workflow of the *"grafting to"* process of binary blends of **Rn** and **Rd11.2** samples. A cleaned silicon wafer covered by a thin native oxide layer (1) is coated with the polymer blend (2) and the *"grafting to*" reaction is then promoted by thermal annealing (3). The unreacted chains are removed by toluene washes (4). The thickness of the brush is determined by ellipsometry whereas the brush composition is obtained by TGA-GC-MS analyses (5). The collected data allow to calculate the grafting densities of deuterated, hydrogenated and total chains (Σ_D, Σ_H and Σ_{TOT} respectively).

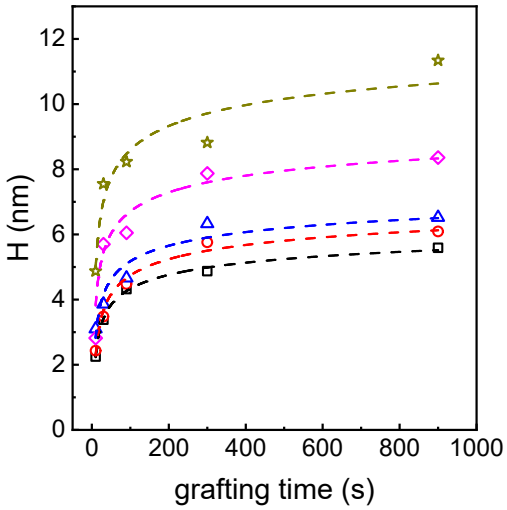

Fig. 4S Layer thickness (H) evolution as a function of time for the equimolar blends of **Rd11.2** and **R3.6** (black), **R5.4** (red), **R8.7** (blue), **R19.9** (cyan) and **R38.6** (dark yellow) grafted to the silicon surface at 250°C. The dashed lines are guides for the eye.

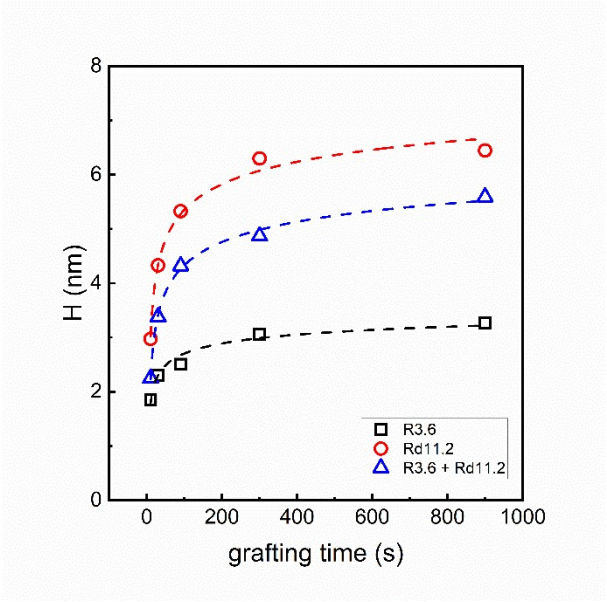

Fig. 5S Layer thickness (H) evolution as a function of time for the equimolar blend of Rd11.2 and R3.6 (blue), as well as those of Rd11.2 (red) and R3.6 (black), grafted to the silicon surface at 250°C. The dashed lines are guides for the eye.

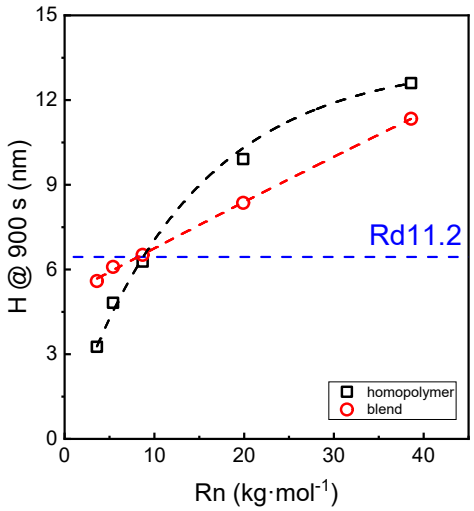

Fig. 6S Trend of the layer thickness (H) of the equimolar blend of Rd11.2 and Rn (red), grafted to the silicon surface at 250°C for 900 s, as well as those of non-mixed Rd11.2 (blue) and Rn (black) grafted under the same conditions.

Deuterated and hydrogenated chain grafting densities calculation.

The total areas of the chromatograms related to the deuterated (m/z = 112) and hydrogenated (m/z = 104) styrene fragments are indicative of the molar amount of the monomers present in the polymer brush and are indicated as $A_{STY\text{-}d8}$ and $A_{STY,}$ respectively.

Since the methyl methacrylate fraction is the same in all the samples (≅ 0.40), the mass fractions of deuterated and hydrogenated polymers in the brush are estimated as

$$f_D = \frac{A_{STY-d8}\,107.2}{A_{STY-d8}\,107.2 + 0.96\,A_{STY}\,102.4} \qquad \text{Eq. 1S}$$

$$f_H = \frac{0.96\,A_{STY}\,102.4}{A_{STY-d8}\,107.2 + 0.96\,A_{STY}\,102.4} \qquad \text{Eq. 2S}$$

where 107.2 g/mol and 102.4 g/mol are the weighted average masses of the monomeric units of the deuterated and hydrogenated polymers and 0.96 is a numerical factor which takes into account the different sensitivity of the mass spectrometer for the deuterated and hydrogenated monomers.

By combining the mass fractions f_D and f_H with the brush thickness H obtained by ellipsometry the grafting densities of the deuterated (Σ_D) and hydrogenated (Σ_H) polymers are calculated using the equations 3S and 4S,

$$\Sigma_D = \frac{f_D\,H\,d\,N_A}{M_{n,D}} \qquad \text{Eq. 3S}$$

$$\Sigma_H = \frac{f_H\,H\,d\,N_A}{M_{n,H}} \qquad \text{Eq. 4S}$$

in which d is the polymer density estimated equal to 1.1 g/cm^3, N_A is the Avogadro's number and $M_{n,D}$ and $M_{n,H}$ are the average molecular weights of the deuterated and hydrogenated polymers, respectively.

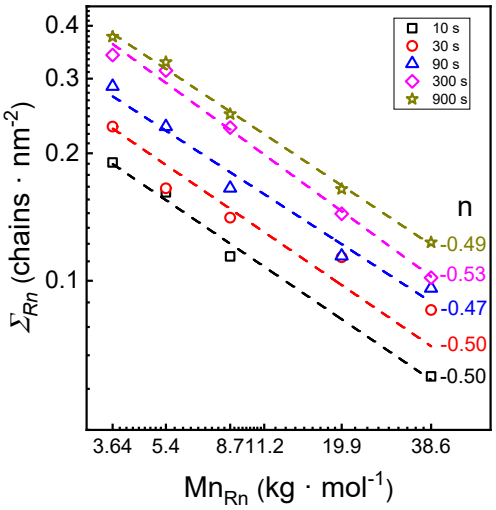

Fig. 7S Grafting density Σ_{Rn} of **Rn** as a function of the molecular weight of Rn for blends of **Rd11.2** with **R3.6** (black), **R5.4** (red), **R8.7** (blue), **R19.9** (cyan) and **R38.6** (dark yellow) grafted to the silicon surface at 250°C at different reaction time. n is the slope of the straight line that fits the data.

Table 1S. List of statistical copolymer chains investigated through the hPF simulations and their mapping into CG representations.

System	N° of Rn chains	N° of Rd11.2 chains	Beads of Rn chains	Beads of Rd11.2 chains	Simulation time (ns)
Rd11.2 – R5.4	753	753	6777	14307	1000
Rd11.2 – R19.9	753	753	24849	14307	1000
Rd11.2 – R38.6	753	753	48945	14307	1000