

Supporting Information: Conformational Changes of a Surface-Tethered Polymer During Radical Growth Probed with Second-Harmonic Generation

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4 **S1. Silanization step**

5 Two kinds of substrates were used. The ones used for the ex-situ sample consisted of glass
6 microscope slides (CAT. NO. 7101, 1-1.2 mm thick, 25.4 x 76.2 mm rectangular), while the
7 substrate of the in-situ sample was a 1 mm thick disc with a diameter of 25 mm. This substrate
8 was made in the universities glassworks from common window glass. The rectangular
9 microscope slide was divided in 7 sections of comparable dimensions by scratching with a glass
10 cutter. These scratches were deep enough to manually break off samples as fast as possible at
11 each sampling event.

12 Prior to the functionalization steps, the substrates were cleaned using a Nochromix® solution
13 for 3 h and a 1 h of UV-ozone oven treatment. Afterwards, each substrate was placed in a plastic
14 vial and reacted with a solution of the polymerization initiator-bearing silane for 1 h. 1 V%
15 silane was used, in 40 mL (4Å-zeolite dried) MeOH, (Sigma-Aldrich, puriss., ACS reagent, ≥
16 99.8%). Each vial also contained four drops of acetic acid (VWR, AnalaR NORMAPUR, 100%),
17 as a catalyst. Then, the slides were rinsed with MeOH, and shaken twice for 15 minutes followed
18 by a drying step in an oven for 1 h at 110° C.

19 **S2. Polymerization procedure**

20 The polymerization protocol is heavily based on the SI-ARGET ATRP protocols of PMMA by
21 Zhu and Edmondson, and Jones and Huck.^{1,2} Firstly the solvent/monomer mixture consisting of
22 32 mL MeOH (Sigma-Aldrich, puriss., ACS reagent, ≥ 99.8%), 8 mL H₂O (distilled water,

1 filtered with Millipore Milli-Q-system ZFMQ 230 04), 40 mg DR1-hexyl methacrylate monomer
2 was purged with argon while stirring for 15 minutes. 4 mL methyl-ethyl-ketone (MEK)(Fischer
3 Scientific, analytical reagent grade) was added to the polymerization solution to enhance
4 dissolution of the monomer. Then, 7.4 mg CuBr₂ (Aldrich Chemistry, 99%), 51.5 mg 2,2'-
5 bipyridine (Sigma-Aldrich, ≥99%), 58.1 mg ascorbic acid (VWR, PROLABO,
6 Ph.EUR./USP/NF) were added followed by intensive argon purging and stirring for 15 minutes.

7 In case of the ex-situ sample, the initiator-silane coated substrate was added to the
8 polymerization solution, followed by argon purging and stirring for 15 minutes. At
9 predetermined synthesis times, a piece of the substrate was broken off from the substrate and the
10 remaining substrate was put back in the polymerization solution. The amount of time the
11 substrate was not in contact with the polymerization solution was minimized. After the sample
12 was placed back in the polymerization solution, the solution was again purged with argon while
13 stirring for 15 minutes. Between the sampling events the reaction vessel was mounted in a
14 shaker. The individual samples were washed by shaking in 8:2:1 v/v/v MeOH/H₂O/MEK for 15
15 minutes, followed by shaking in THF (Sigma-Aldrich, ACS reagent, ≥99.9%) for 15 minutes
16 and drying with compressed air.

17 In case of the in-situ sample, the substrate was mounted in a home-made SHG-measurement
18 cell. The cell was purged with argon for 5 minutes followed by insertion of 2 mL of the
19 polymerization solution. The cell was then fixed in the SHG-setup. After the measurement, the
20 sample was washed by shaking in 8:2:1 v/v/v MeOH/H₂O/MEK for 15 minutes, followed by
21 shaking in THF for 15 minutes and drying with compressed air.

22

S3. Synthesis of the initiator-functionalized silane

The silane used in the silanization step was synthesized by reacting 1.3 equivalents (0.338 mL) of 3-mercaptopropyltrimethoxysilane (Sigma-Aldrich, 95%) with 1 equivalent (0.3 mL) of 2-(2-bromoisobutyryloxy)ethyl methacrylate (Sigma-Aldrich, 95%) and 5 mol% of 2,2-dimethoxy-2-phenylacetophenone (Sigma-Aldrich, 99%). This method was adopted from Bloemen et al.³

S4. DR1-hexyl methacrylate monomer

The monomer, (E)-6-(ethyl(4-((4-nitrophenyl)diazenyl))phenyl)amino)hexyl methacrylate), was prepared by the Laboratory of Polymer Synthesis (KU Leuven). Compared to Disperse Red 1 (DR1), the used chromophore differs in the length of the linker group between hydroxyl-end and the tertiary amine. In case of the synthesized monomer, a hexyl-linker is located between the methacrylate function and the tertiary amine located on the chromophore. The chemical structure of the monomer is shown in Fig. S1.

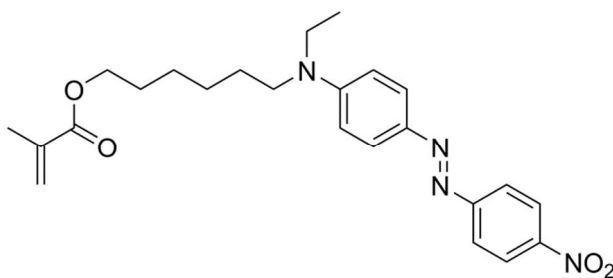


Figure S1. The Disperse Red 1 functionalized methacrylate monomer used in the polymerization.

S5. Optical measurements: SHG

All SHG-measurements in this work were performed using a SHG-setup with lock-in detection (SR 830 in combination with a home-built mechanical chopper at 770 Hz), and the detection was

performed in the reflection geometry at 45° to the surface normal of the sample. The laser was a Ti-sapphire (Spectra Physics, Tsunami®) femtosecond laser operating at 800 nm. All SHG measurements are corrected for fluctuations in the laser stability and pulse width by taking the ratio with the SHG from a reference sample, a slab of quartz.⁴ A combination of a polarizer (Thorlabs, GL10-B) and a half-wave plate (Thorlabs, WPH05M-808) was used to limit the laser output power to 250 mW average power. A second half-wave plate was used to change the polarization direction of the fundamental laser light. Further details of the SHG-setup can be found elsewhere.^{4,5} The solvent used for the ex-situ grafted sample was 8:2:1 v/v/v MeOH/H₂O/MEK.

The ex-situ samples taken at 4 h and 7 h broke in two triangular pieces after breaking them off the main substrate, therefore in order to measure from both pieces (without major relocation of the sample holder or laser beam path), one of the samples had to be rotated. Both pieces generated a similar NLO signal and polarization dependency, as is shown by their small error bars in figure 2 (main text).

The polarized SHG data of the 8 h ex-situ sample was measured on two occasions, separated by a period of one week. Under the assumption of a narrow tilt angle distribution, the average tilt angle was determined at $56.6 \pm 0.1^\circ$. The average tilt angles of the ex-situ sample, under assumption of a narrow distribution, are plotted in figure S3. The supplied errors originate from the errors of the fitting procedure that determined the values of the contributing tensor components. The polarized SHG data were fitted to a $C_{\infty v}$ model.⁶⁻⁸ A typical fit is shown in figure S2 for the 3 h ex-situ sample. Possible contribution due to scattering were not taken into account.

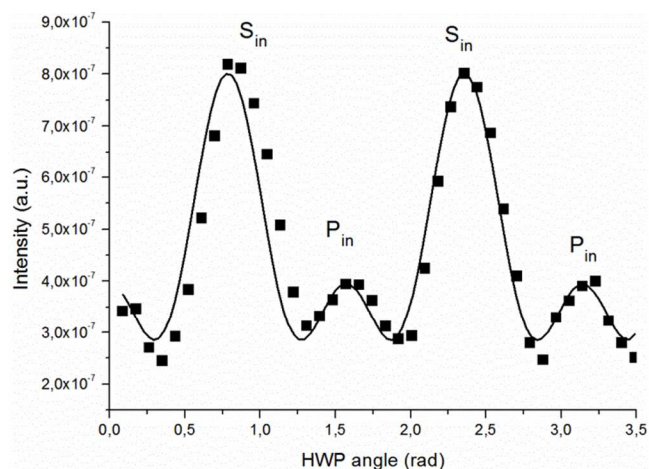


Figure S2. A typical fit of the P-polarized SHG data.

The progress of the polymerization of the in-situ sample was evaluated by measuring the P-polarized SHG-response on three positions (0.5 mm separated from each other) on the substrate at as many time intervals as possible. The measurement error is provided for the series presented in figure 2 in the main text. The recorded SHG-signals are plotted in Fig. S3

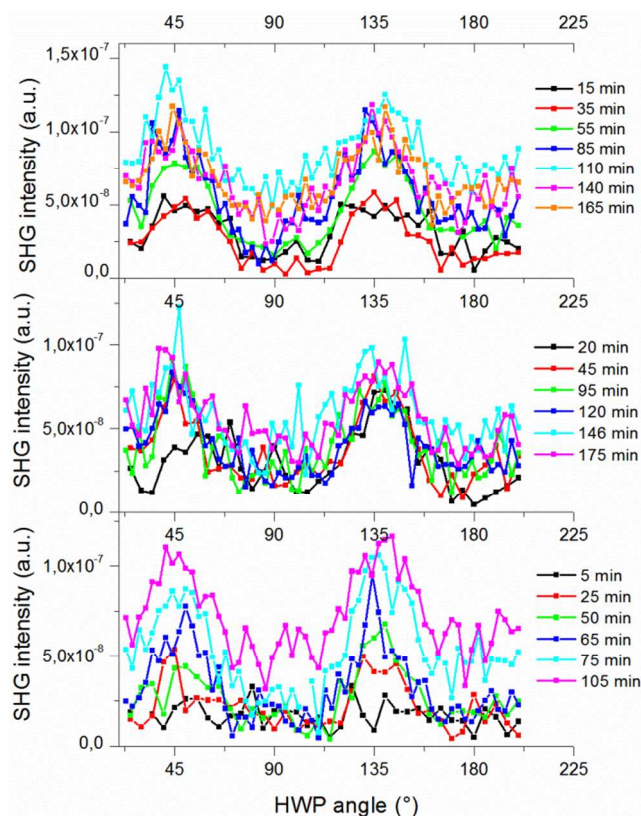


Figure S3. The P-polarized SHG-signals from the in-situ sample, taken from the three positions on the substrate.

The nonlinear optical data of each of these positions was used to calculate the average molecular tilt angle under the assumption of a narrow distribution.⁹ Because of the different experimental geometry compared to the ex-situ sample (see Fig. 1, main text), the Fresnel coefficients used in the calculation of the average tilt angle were adapted.⁸ As can be seen in Fig. S4, the average tilt angles on each measurement position are comparable and show a comparable trend with polymerization time. The errors are calculated from the errors on the values from the fitting procedure.⁷

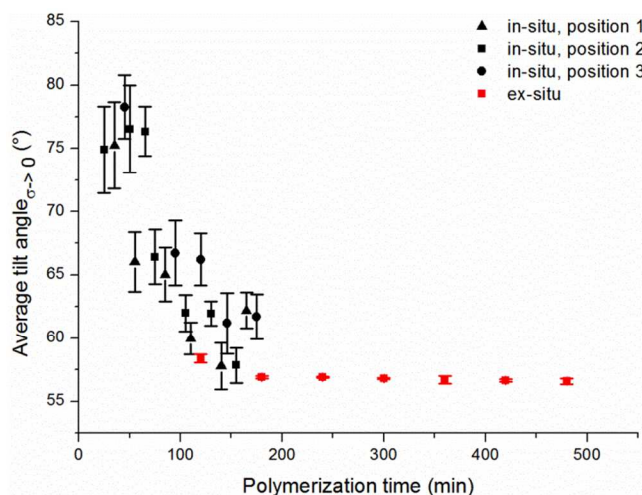


Figure S4. The average molecular tilt angles under the assumption of a narrow-distribution of both polymer samples.

S6. Optical measurements: UV-Vis

The samples were fixed in a holder for microscope glass which was perpendicularly aligned to the collimated light beam. The UV-Vis spectrometer is a Perkin Elmer Lambda 900. Prior to the measurement, a baseline was taken with a freshly cleaned substrate. All samples showed an increase in absorbance with polymerization time due to the increased thickness of the grafted layers, except the ex-situ sample at 8 h polymerization time. The measured UV-Vis spectra of the ex-situ sample and the in-situ sample are plotted in Fig. S5. The poly(DR1-hexyl polymer) shows the expected absorption band characteristic for the chromophore absorbance. Note that the in-situ grafted polymer sample only contains polymer on one side hence its low absorbance value in Fig. S5. In Fig. S6, an example of the determination of the wavelength of maximal absorbance is provided, by the 3 h ex-situ sample.

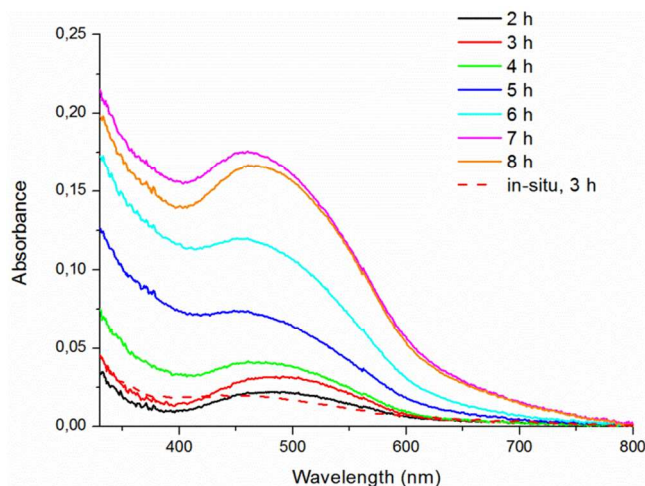


Figure S5. The absorbance spectra of the in-situ and ex-situ grafted DR1-modified polymer.

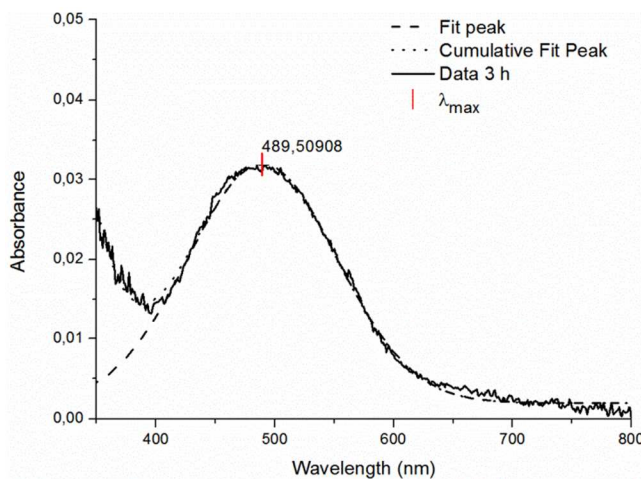


Figure S6. Determination of the wavelength of maximal absorbance for the 3 h ex-situ sample.

S7. Thickness measurements: AFM

The thickness of the polymer brushes was determined using Atomic Force Microscopy (AFM). The microscope was a Quesant Q-scope® operating in intermitted contact imaging mode (tapping mode). The probe tip was a NSC16 (Quesant Instrument Corp) with a force constant of 40 N/m and a resonance frequency of 0.170 kHz. In order to probe the thickness of the sample, pieces of thin cover glass were used to manually scratch the polymer layer. Care was taken not to scratch the glass substrate. For both samples, 5 scans were taken (for each polymerization time),

and from each scan, 7 thickness values were obtained and averaged after digital sample leveling performed by the measurement software. We were unable to probe the thickness of the silane layer.

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