Electronic Supplementary Information

Visualization of poly(methyl methacrylate) (PMMA) grafts on cellulose *via* high-resolution FT-IR microscopy imaging

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Experimental Section

Materials

α-Bromoisobutyryl bromide (BiB, 98%), 4-(dimethylamino)pyridine (DMAP, 99%), ethyl 2-bromoisobutyrate (EBiB, 98%), copper(II) bromide (Cu(II)Br_2, 99%), *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (PMDETA, 99%) and Whatman No. 1 filter paper were purchased from Sigma Aldrich. Ascorbic acid (AsAc, 99%) was purchased from Fluka. Triethylamine (TEA) was purchased from Merck. Methyl methacrylate (MMA, 99%, Sigma Aldrich) was passed through a column of neutral aluminum oxide (Al_2O_3, Sigma Aldrich) prior to use in order to remove the inhibitor. Ethanol (96 %, VWR), acetone (99.9 %, VWR), tetrahydrofuran (THF, 99.9 %, Sigma Aldrich), anisole (99 %, Fluka) were used as received.

Instrumentation

NMR Spectroscopy. ^{1}H-NMR spectra were recorded on a Bruker Avance 400 MHz NMR instrument, using $CDCl_3$ as solvent. The solvent residual peak was used as internal standard.

Size Exclusion Chromatography (SEC). SEC using THF (1.0 mL min^{-1}) as the mobile phase was performed at 35 ºC using a Viscotek TDA model 301 equipped with two T5000 columns with porous styrene divinylbenzene copolymer (length: 300 mm; inner diameter: 7.8 mm; exclusion limit MW polystyrene: 400,000,000 Da) from Malvern (UK), a VE 2500 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser from Viscotek Corp. (The Netherlands). A conventional calibration method was created using narrow linear poly(methyl methacrylate) standards (MW ranging from 805-400,000 Da). Corrections for the flow rate fluctuations were made by using toluene as an internal standard. Viscotek OmniSEC version 4.0 software was used to process data.

FT-IR Measurements and FT-IR Microscopy Imaging. Infrared measurements of the cellulose samples have been performed using a Bruker FT-IR microscope HYPERION 3000 coupled to a research spectrometer VERTEX 80. The HYPERION 3000 microscope is equipped with two types of detectors: a single element MCT-detector (Mercury Cadmium Telluride) for the conventional mapping approach and a multi-element FPA-detector (Focal Plane Array) for imaging. The multi-element FPA-detector consists of 64×64 elements. This fact allows for the simultaneous acquisition of 4096 spectra covering a sample area of 32×32 µm (for ATR detection). With the FPA-detector in combination with the 20× Germanium ATR-lens, a lateral resolution of 0.25 μm^2 per pixel is achieved. This high resolution is needed for the analysis of single fibers within the cellulose matrix in order to examine the homogeneity of the covalent functionalization applied on the cellulose. Beside the high lateral resolution, the extremely short measurement time is another significant benefit of the FPA-detector. With the FPA-detector, 4096 spectra are acquired simultaneously within a few seconds. For post-processing, baseline correction and atmospheric compensation were used.

Field-Emission Scanning Electron Microscope (FE-SEM). FE-SEM micrographs were recorded on a Hitachi S-4800 FE-SEM. The samples were mounted on a substrate with carbon tape and coated 3 s of a carbon coater (Cressington 108carbon/A) and subsequently 2×4 nm of a gold/palladium sputter coater (Cressington 208HR).

Immobilization of α-bromoisobutyryl bromide on cellulose. The procedure for immobilization of initiator on the cellulose surface was adopted from Carlmark and Malmström.[1] Prior to the immobilization of the initiator, the filter paper (2×3 cm) was thoroughly washed with ethanol, acetone, and tetrahydrofuran (THF) and additionally ultrasonicated for 2 min in each solvent. The available hydroxyl groups on the surface were converted into ATRP initiators by immersing the filter paper in a solution containing BiB (305 mg, 1.33 mmol), TEA (148 mg, 1.46 mmol), and a catalytic amount of DMAP in THF (20 mL). The reaction was allowed to proceed for 4 h at ambient temperature on a shaking device. Thereafter, the filter paper was thoroughly washed in THF and ethanol, in order to remove residual reactants and by-products. The filter paper was finally dried in a vacuum oven at 50 °C over night.

Polymerization of MMA from cellulose *via* ARGET ATRP. The initiator-functionalized paper (2×3 cm) was immersed into a 25 mL round-bottomed flask containing anisole (10 g), MMA (10 g, 0.10 mol), EBiB (39.4 mg, 0.13 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA) (21.7 mg, 0.13 mmol), $Cu(II)Br_2$ (2.8 mg, 13 µmol), and ascorbic acid (AsAc) (22.0 mg, 0.13 mmol), targeting the final DP_n of 800, as described previously.[2] For the two system targeting a DP_n of 1500, where one contained 1.25 times more of the ligand, catalyst, and reducing agent, the amounts were: anisole (10 g), MMA (10 g, 0.10 mol), EBiB (13.0 mg, 0.067 mmol), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA) (11.5 mg, 0.067 mmol; 14.4 mg, 0.084 mmol), $Cu(II)Br_2$ (1.5 mg, 6.7 µmol; 1.9 mg, 8.4 µmol), and ascorbic acid (AsAc) (11.7 mg, 0.084 mmol; 14.6 mg, 0.084 mmol), respectively. The flask was sealed with a rubber septum and purged with argon for 5 min in an ice-bath, before being placed in a thermostatted oil bath at 40 °C. The reaction was monitored with ^{1}H-NMR and terminated when the desired conversion was reached by exposing the reaction mixture to air and by diluting it with DCM. The free polymer was purified by precipitation. The filter paper

was thoroughly washed in DCM, THF, THF:H_2O (1:1), H_2O, methanol, and ethanol. Finally, the sample was dried in a vacuum oven at 50 ºC over night.

FT-IR microscopy analysis

The cellulose-fiber topography can be displayed by integration of the characteristic absorption intensity of cellulose that ranges from 950 to 1200 cm^{-1}, corresponding to the cellulose signal of C-O stretching vibration (Figure S1).

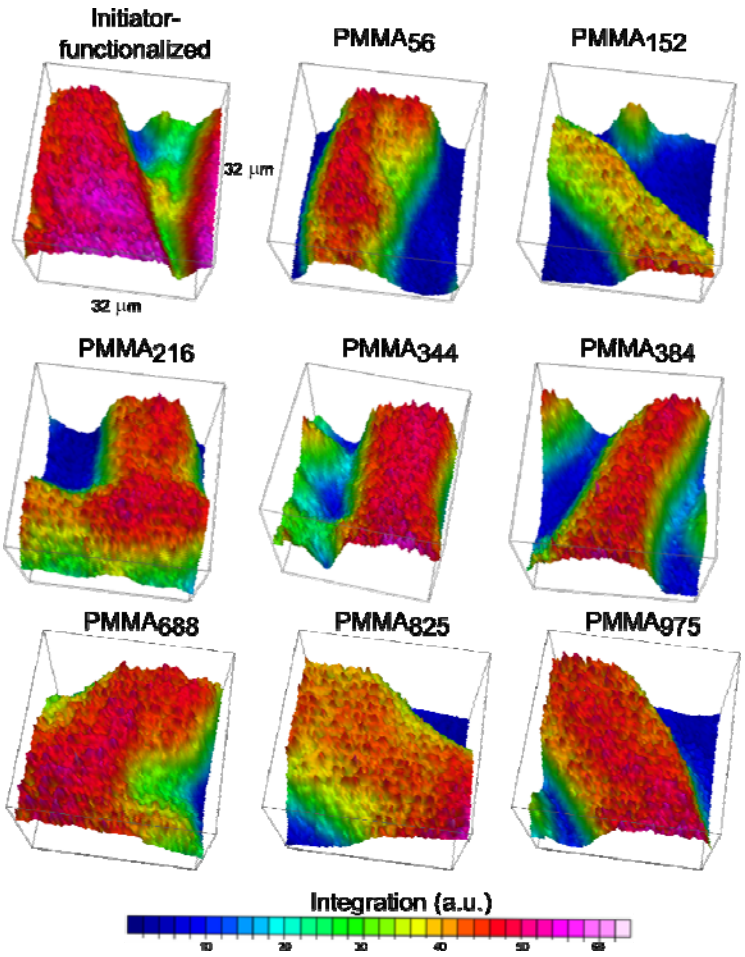

Fig. S1. False color high resolution FT-IR micrographs (4 cm^{-1} spectral resolution with a 0.25 μm^2 spatial pixel resolution and an optical resolution of close to 1 µm) displaying the cellulose fibers located via their IR signal by integration of the region 950-1250 cm^{-1}.

To further visualize the cellulose fibers, FE-SEM was employed, and the micrograph of the $PMMA_{384}$-grafted cellulose fiber can be seen in Figure S2.

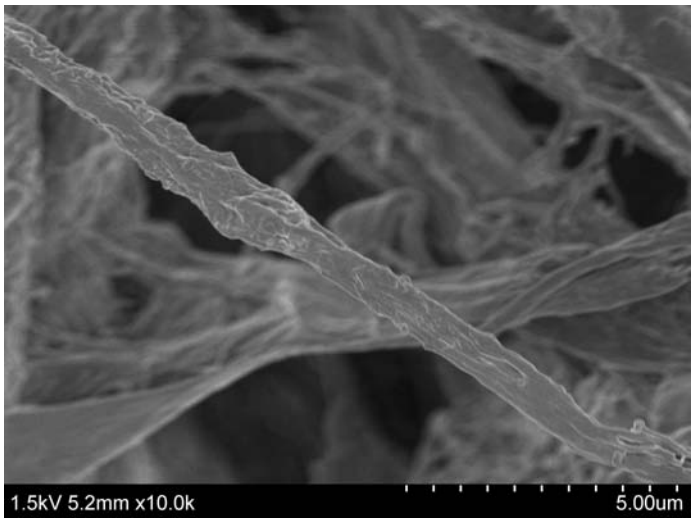

Fig. S2: The FE-SEM micrograph of the $PMMA_{384}$-grafted cellulose fiber.

The average spectra of the FT-IR micrographs of the PMMA-grafted cellulose can be seen in Figure S3, indicating an increase in intensity with increasing graft length which corroborates the results from the false color FT-IR micrographs (Figure 1).

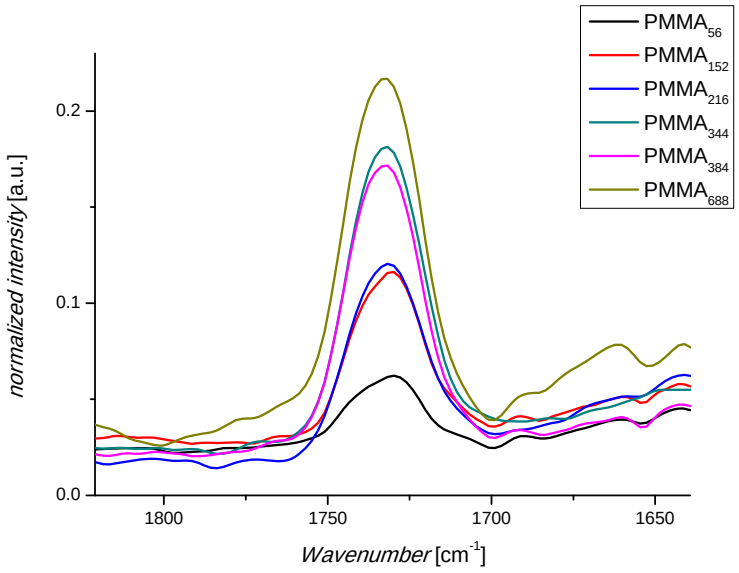

Fig. S3: The average spectra of the FT-IR micrographs showing an increase of the carbonyl stretching vibration with increasing degree of polymerization. The spectra were obtained by averaging 13×13 spectra in a square of ~10.5 μm^2 on the cellulose surface.

References

1 Carlmark, A.; Malmström, E. *J. Am. Chem. Soc.* **2002**, *124*, 900-901.
2 Hansson, S.; Östmark, E.; Carlmark, A.; Malmström, E. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2651-2659.