Experimental Section

Materials

All solvents and chemicals were commercially available, and unless otherwise stated, were used as received. DMAc, LiCl, NaH and NaOH were purchased from Acros Organics, propargyl bromide was purchased from Alfa Aesar. Microcrystalline cellulose and triethylamine were purchased from Sigma–Aldrich.

Instrumentation

Microwave irradiations were performed by the means of an Ethos 1600 MicroSynth reactor from Milestone. The temperature was measured with a optic-fibre thermometer (ATC-FO)/Ethos.

^{1}H NMR (^{13}C NMR) spectra were recorded at 400.13 MHz (100.62MHz) with a Bruker DPX spectrometer using DMSO-d6 and $CDCl_3$. Chemical shifts (δ) are expressed in ppm with Me_4Si as the internal standard (δ0).

A Perkin Elmer 1000 FTIR spectrometer equipped with the Spectrum software was used to perform FTIR analysis. The spectra were obtained by preparing dried KBr powder pellets containing 5 % w/w of the investigated sample.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that provides elemental composition information of a pellet composed of homogeneous grind sample to a depth of a few nanometres. A Kratos Axis Ultra spectrometer was used to evaluate the atomic concentrations present on the functionalised surface from the integral of elemental peaks intensities. Three trials were completed for each sample.

Synthesis

Dissolution of cellulose in DMAc/LiCl

Cellulose (30 g) is suspended in MeOH (100 mL) for 30 min while stirring at room temperature. Suspension is filtered; afterwards cellulose is suspended in DMAc (100 mL), in the same conditions. Then, the suspension is filtered again. In parallel, LiCl (105 g) is dissolved in DMAc (1.5 L) at 70 °C. When LiCl is dissolved, pre-treated cellulose is dissolved in DMAc/LiCl solution at 70 °C over 4 hours.

Dissolution of cellulose in aqueous NaOH

Typically one gram of cellulose was suspended in 26.9 mL of water. 2.5 g of NaOH was then added, and the mixture was shaken to dissolve the NaOH at room temperature, resulting in a suspension of the cellulose in an 8.5 % NaOH solution. The suspension was cooled to -18 °C and held at that temperature until it became a solid frozen mass. The frozen solid was then allowed to thaw at room temperature, and was transformed into a gel-like mass. Water (20.6 ml) was added to the gel-like material and, with gentle shaking, and a clear cellulose solution was obtained. The resulting solution contained 2 % cellulose in 5 % aqueous NaOH.

Preparation of propargylcellulose with NaH in DMAc/LiCl at room temperature

To 100 mL of DMAc/LiCl cellulose solution (2 g, 12.4 mmol), 3.72 g (62.0 mmol, 5 equiv) of sodium hydride was carefully added before adding 6.68 mL (62.0 mmol, 5 equiv) of propargyl bromide. After stirring for 7 days at room temperature, water (50 mL) was added slowly to destroy the excess of NaH. The mixture was then poured into distilled water (300 mL) and the precipitate was filtered off and washed with hot distilled water (300 mL) and hot EtOH (150 mL). The product was dried at 50 °C under vacuum (900 mg, mass yield: 45 %, DS: 0.18).

Preparation of propargylcellulose with NaH in DMAc/LiCl under microwave activation

To 100 mL of DMAc/LiCl cellulose solution (2 g, 12.4 mmol), 3.72 g (62.0 mmol, 5 equiv) of sodium hydride was carefully added. A first microwave activation was realized (2 x 1’, 300 W, 75 °C) before adding 6.68 mL (62.0 mmol, 5 equiv) of propargyl bromide. After microwave activation (10 x 1’, 300 W, 75 °C), water (50 mL) was added slowly to destroy the excess of NaH. The mixture was then treated like the precedent reaction (1.64 g, mass yield: 82 %, DS: 0.45).

Preparation of propargylcellulose with NaOH in DMAc/LiCl under microwave activation

To 100 mL of DMAc/LiCl cellulose solution (2 g, 12.4 mmol), 1.12 g (55.8 mmol, 4.5 equiv) of ground sodium hydroxide was added. A first microwave activation was realised (2 x 1’, 300 W, 75 °C) before adding 6.68 mL (62.0 mmol, 5 equiv) of propargyl bromide. After a second microwave activation (10 x 1’, 300 W, 75 °C) and cooling to room temperature, the mixture was poured into distilled water (300 mL) and the precipitate was filtered off and washed with hot distilled water (300 mL) and hot EtOH (150 mL). The product was dried at 50 °C under vacuum (1.50 g, mass yield: 75 %, DS: 0.44).

Preparation of propargylcellulose in aqueous NaOH

To 95 mL of aqueous NaOH cellulose solution (2 g, 12.4 mmol), propargyl bromide was added. After stirring at room temperature or after microwave activation and cooling to room temperature, the mixture was poured into both distilled water/EtOH v/v (50/50 mL) and the precipitate was filtered off and washed with hot distilled water (300 mL) and hot EtOH (150 mL). The product was dried at 50 °C under vacuum.