Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Hybrid silica micro-particles with light-responsive surface properties and Janus-like character

A. Romano,[a] M. Sangermano[a]†, E. Rossegger,[b] I. Mühlbacher,[b] T. Griesser,[c] M. Giebler,[b] G. Palmara,[a] F. Frascella,[a] I. Roppolo,[a] and S. Schlögl,[b]

[a]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*

[b]*Institute of Chemistry of Polymeric Materials, Montanuniversitaet Leoben, Otto Glöckel-Strasse 2, A-8700 Leoben, Austria*

[c]*Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, A-8700 Leoben, Austria*

Results and Discussion

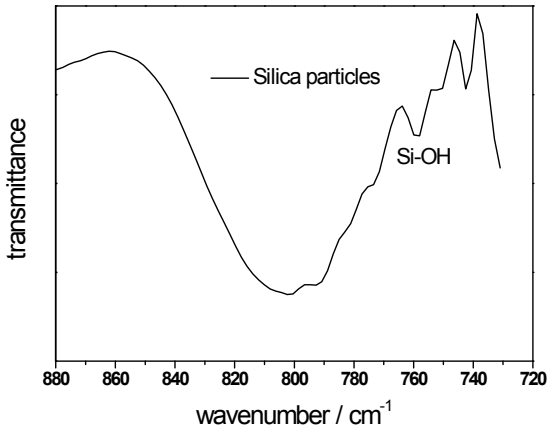

Figure S1 – IR bands of the characteristic silanol groups (Si-OH) magnified out of the FT-IR spectrum of silica micro-particles after RCA-SC1 chemical treatment protocol using hydrogen peroxide and ammonium hydroxide.

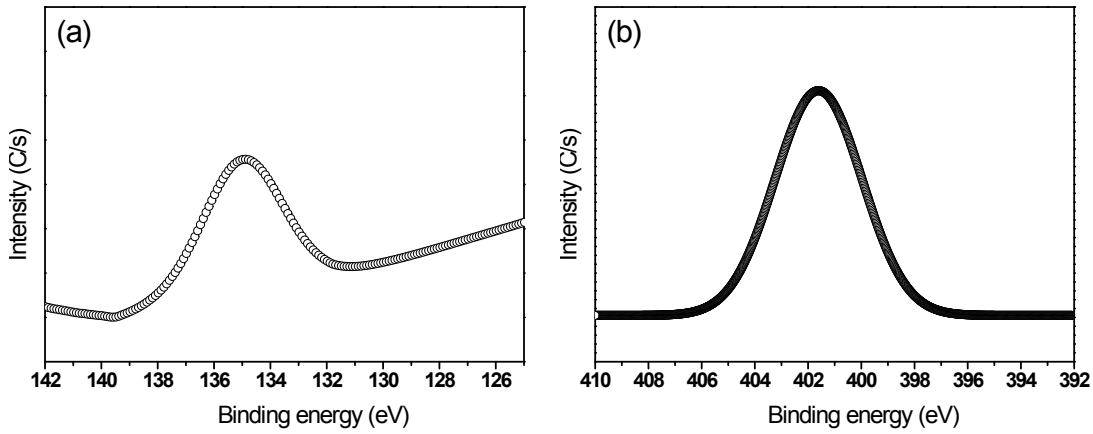

Figure S2 – (a) High-resolution P2p spectrum of silica particles modified with TMESI[2]-BAPO. (b) High-resolution N1s spectrum of silica particles modified with 3-APTMS.

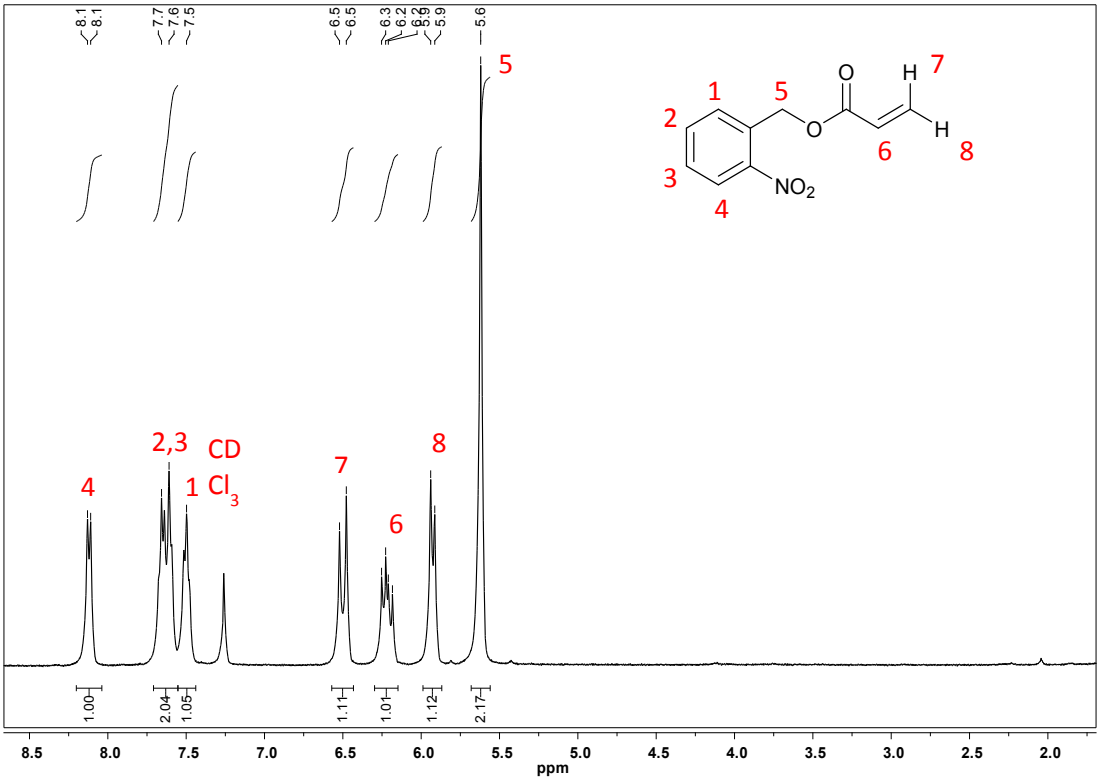

Figure S3 – ^{1}H NMR spectrum of mono-acrylate-**NBE**

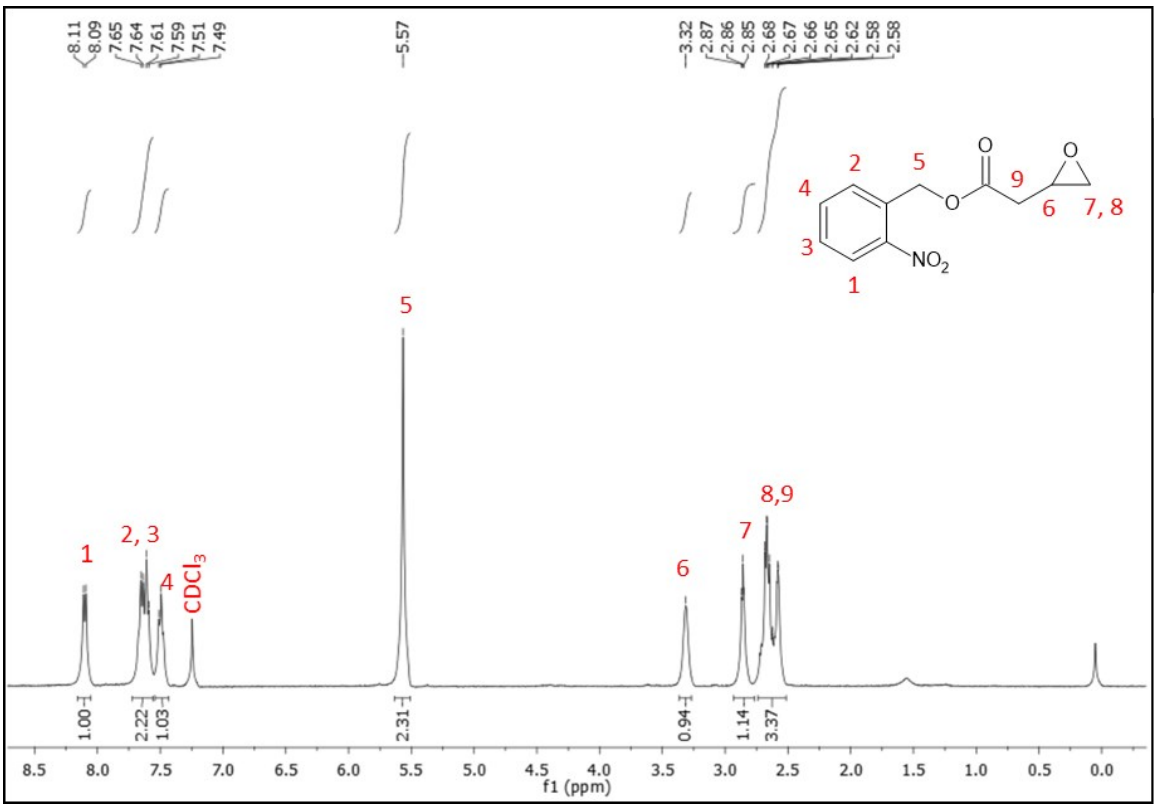

Figure S4 – ^{1}H NMR spectrum of mono-epoxy-**NBE**

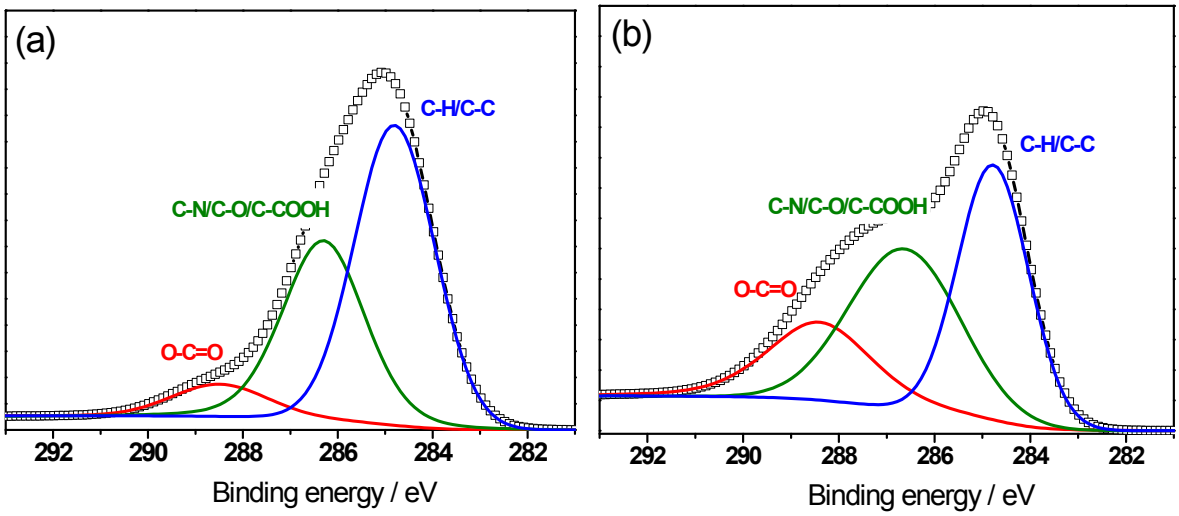

Figure S5 – Deconvoluted high-resolution C1s spectra of thermally grafted silica particles (a) prior to and (b) after UV-induced cleavage.

Experimental

Surface modification of glass slides with TMESI²-BAPO

The silanization of glass slides with TMESI²-BAPO followed the same procedure as adopted for the silica micro-particles, in terms of time and solvent to silane ratio. The cleaned slides were placed in a glass flask with one surface exposed to a solution of 25 mL of acetonitrile (99.99%) and 300 mg of TMESI²-BAPO. Subsequently, the flask was closed, and inert atmosphere was attained carrying out 3 cycles of vacuum/nitrogen atmosphere. The silanization proceeded for 48 h at room temperature and finally, the slides were collected and washed 5 times in acetone in a sonication bath.

Surface modification with amino-functional organosilane

The modification of glass slides with 3-APTMS followed the same procedure as adopted for the silica micro-particles, in terms of time and solvent to silane ratio. The cleaned slides were placed in a glass flask with one surface exposed to a solution of 25 mL of toluene (99.98%) and 300 mg of 3-APTMS. Subsequently, the flask was closed, and inert atmosphere was attained carrying out 3 cycles of vacuum/nitrogen atmosphere. The silanization proceeded up to 12 h in oven at 80 °C, and finally the slides were collected and washed 2 times in toluene and 3 times in acetone in a sonication bath.

"Photo-induced grafting-from" ***procedure***

The "photo-grafting from" protocol followed the same procedure employed for silica micro-particles in terms of time and solvent to monomer ratio. Particularly, the TMESI²-BAPO silanized glass slides were placed in an opened petri dish with the modified surface exposed to a solution of 2 mL of

acetonitrile (99.98%) and 125 mg of mono-functional mono-acrylate-**NBE**. Subsequently, the petri dish was closed and inert atmosphere was obtained by carrying out 3 cycles of vacuum/nitrogen atmospheres. The sample was then irradiated for 4 hours with a medium pressure mercury lamp: Omnicure series 1500, equipped with an optical waveguide and interposing an external cut-off ($\lambda < 400$ nm) (filter Newport Corporation (UV filter - Color Glass Filter. 25.4 mm DIA, GG400 cut-off $\lambda < 400$ nm) between the lamp fibre and the chamber (visible light intensity amounted to 350 mW/cm^2). Finally, the slides were collected and washed 5 times in acetone by means of sonification bath.

Thermal* "grafting-from" *procedure

The grafting-from protocol followed the same procedure employed for the silica micro-particles in terms of time and solvent to monomer ratio. The 3-APTMS silanized glass slides were placed in flask with the modified surface exposed to a solution of 2 mL of toluene (99.98%) and 125 mg of mono-functional mono-epoxy-**NBE**. Subsequently, the flask was closed and inert atmosphere was attained by carrying out 3 cycles of vacuum/nitrogen atmosphere. The samples were heated to 65 °C in an oven for up to 24 h and were kept overnight at room temperature (14 h). Finally, the slides were collected and washed 2 times in toluene and 3 times in acetone by means of sonification bath.

UV-cleavage of polymer brushes

The grafted samples were placed in flask with the grafted surface exposed to a solution of 1.75 mL of acetonitrile (99.98%) and inert atmosphere was attained by carrying out 3 cycles of vacuum/nitrogen atmosphere. The samples were then UV irradiated with a medium pressure mercury lamp for 30 minutes: Omnicure series 1500, equipped with an optical waveguide (intensity: UVA 180 mW/cm^2, UVB 32 mW/cm^2, UVC 19 mW/cm^2, UVV 400 mW/cm^2). Finally, the slides were collected and washed 5 times in acetone by means of sonification bath.