

Supporting Information

Adding stimuli-responsive extensions to antifouling hairy particles

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Experimental section

Materials. 2-(Dimethylamino) ethyl methacrylate (DMAEMA) was purified by passing over a basic alumina column. Sodium methacrylate (NaMA) (99%, Aldrich), copper (I) bromide (Cu(I)Br) (98%, Aldrich), 2,2'-bipyridine (bpy) (99%+, Aldrich) were used as received. The dialysis tubing (with cut-off molecular weight of 3500) was purchased from Serva. Bovine albumin-fluorescein isothiocyanate conjugate was supplied by Sigma-Aldrich.

Surface initiated ATRP of DMAEMA from hairy particles. The functionalized polystyrene hairy particles were synthesised and characterised as previously reported.¹ A suspension of functionalised hairy particles in water (2 g, 16.6 wt % solids) previously dialysed was de-oxygenated for 20 min with nitrogen in a Schlenk tube fitted with a magnetic stirring bar. The tube was charged with bpy (0.0198 g, 127 μmol) and Cu(I)Br (0.0091 g, 64 μmol) and the mixture was purged with nitrogen under stirring. The monomer, DMAEMA, (1 g, 6.36 mmol) was added subsequently to the reaction which was heated at 45 °C. Samples were taken periodically from the mixture at suitable time periods and conversion measured by gravimetry. After 7 h the polymerisation was stopped and purified by dialysis to remove the residual monomer and the catalyst.

A control experiment (using a non-dialysed seed latex) was carried out under the same experimental conditions but in the absence of the Cu/bpy system.

Surface initiated ATRP of NaMA from hairy particles. A suspension of the seed hairy particles in water (2 g, 16.6 wt % solids) previously dialysed was placed into a Schlenk tube. Sodium methacrylate (1 g, 9.26 mmol) was added to the suspension and the pH of the medium was adjusted to pH = 9. The mixture was deoxygenated by purging with nitrogen for 20 min at ambient temperature. Subsequently, bpy (0.0289 g, 185 μ mol) and Cu(I)Br (0.0133 g, 93 μ mol) were added to the reaction. The polymerisation was allowed to proceed for 5 h at room temperature under nitrogen atmosphere. The resulting latex was cooled in an ice bath and purified by dialysis. The monomer conversion of the final latex was determined by gravimetry, removing the residual monomer by dialysis.

Measurements. FTIR spectra were recorded on a Bio-Rad Infrared Excalibur 3000 FTIR spectrometer. The particle size distributions were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS instrument at 25 °C. Malvern Dispersion Software was used for data acquisition and analysis, applying the general purpose algorithm for calculating size distribution. The analysis of the mean electrophoretic mobility was also performed using a Malvern Zetasizer Nano ZS instrument at 25°C. The zeta potential was calculated from the mean electrophoretic mobility through Smoluchowski's equation. Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM instrument (with a LaB₆ filament, operating voltage=200 kV). The particle size distributions were obtained from statistical treatment of representative TEM images for each sample using the software ImageJ (<http://rsb.info.nih.gov/ij/>). Average particle diameters and polydispersities (PDI_{TEM}) were determined from these particle size distributions. PDI_{TEM} were calculated according to $PDI = D_w/D_n$ where D_w is the weight average diameter, $D_w = \sum n_i D_i^4 / \sum n_i D_i^3$ and D_n is the number average diameter $D_n = \sum n_i D_i / n_i$ (n_i is the number of particles with diameter D_i). The films studied by contact angle and fluorescence spectroscopy methods were deposited as thin films on glass or aluminum surfaces. Films used for contact angle measurements were annealed at 130

°C for 24 h. Contact angles were measured using deionized water on a Dataphysics OCA 30 instrument at room temperature. Dynamic advancing and receding contact angles were recorded while water was added to and withdrawn from the drop, respectively, by a syringe pump. Non-specific adsorption of proteins (i.e, bovine albumin serum) on functionalized polystyrene films was studied by incubating the samples in buffered saline solution (PBS, pH = 7.4) of 1 mg mL^{-1} of BSA-FITC. After 24 h, non-absorbed proteins were removed by washing the films with excess PBS and distilled water. The relative fluorescence intensity, which was taken as a measure for the amount of adsorbed protein, was determined by steady-state fluorescence spectroscopy using an Edinburgh Instruments FS920. Emission spectra were recorded from 500 to 800 nm using excitation light of 490 nm.

Results.

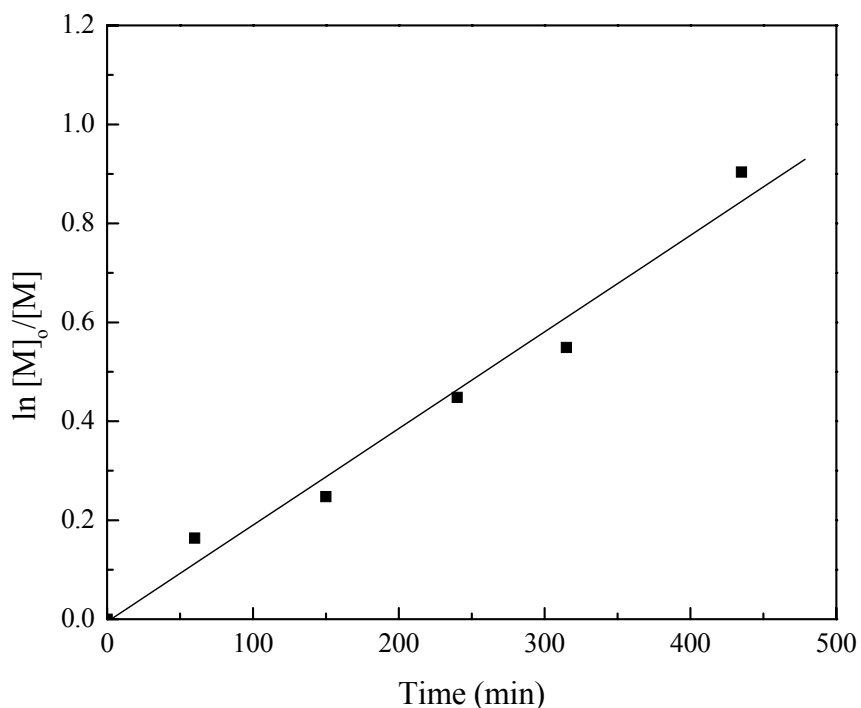


Figure S1. First-order kinetic plot for the surface initiated ATRP of DMAEMA from the hairy particles at 45 °C.

Characterization of the particles after adding extensions of PDMAEMA and PNaMA by FTIR.

The ATRP of DMAEMA from polystyrene hairy particles was investigated by FTIR as shown in Figure S2. The characteristic absorption band at 1112 cm^{-1} (C-O-C stretching vibration) is consistent with the presence of P(PEGMA) in the polystyrene latex. After the chain extension of DMAEMA from the polystyrene latex stabilised by $\text{PS}_{40}\text{-}b\text{-P(PEGMA1100)}_{70}$, an absorption band at 2770 cm^{-1} corresponding to C-H stretching of the tertiary amine moiety of PDMAEMA was appears. Also a very clear absorption band at 1730 cm^{-1} corresponding to ester C=O stretching of PDMAEMA is observed.

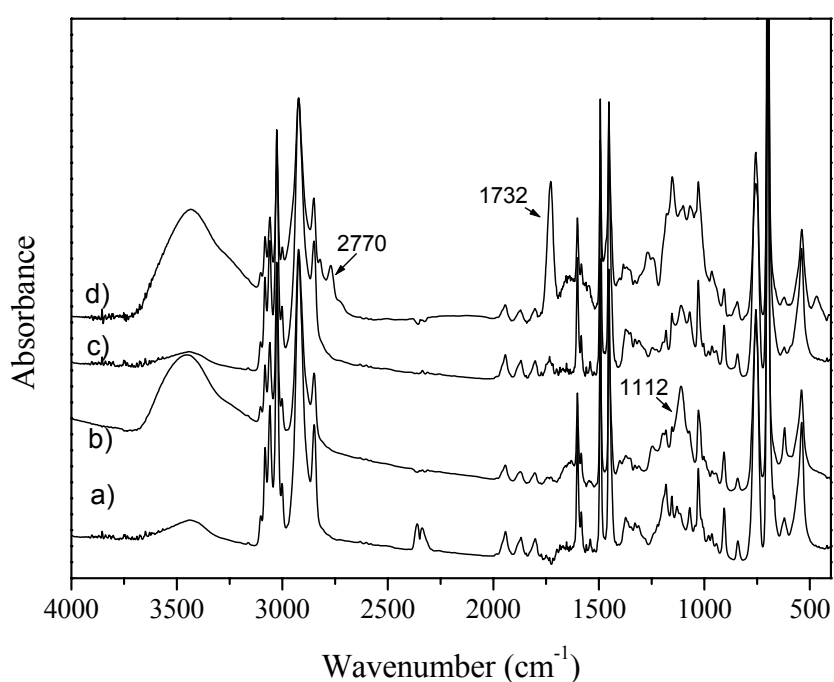


Figure S2. FTIR spectra of a) polystyrene latex, b) polystyrene latex stabilized by $\text{PS}_{40}\text{-}b\text{-P(PEGMA1100)}_{70}$, c) polystyrene latex after the polymerization in the absence of CuBr/bpy (control experiment), d) polystyrene latex after extension with PDMAEMA.

The successful chain extension of NaMA was also investigated by FTIR as shown in Figure S3. The characteristic absorption band at 1112 cm^{-1} (C-O-C stretching vibration) is consistent with the presence of P(PEGMA) in the polystyrene latex. After the ATRP of NaMA from the polystyrene latex stabilized by $\text{PS}_{40}\text{-}b\text{-P(PEGMA1100)}_{70}$, the antisymmetric OC-O valence band caused by the sodium salt of poly(methacrylic acid) is seen at 1548 cm^{-1} . After the conversion of sodium methacrylate salt into carboxylic acid groups a new absorption appears at 1700 cm^{-1} , typical of the carboxylic acid moieties and characteristic for hydrogen-bonded dimers of carboxylic acid groups.

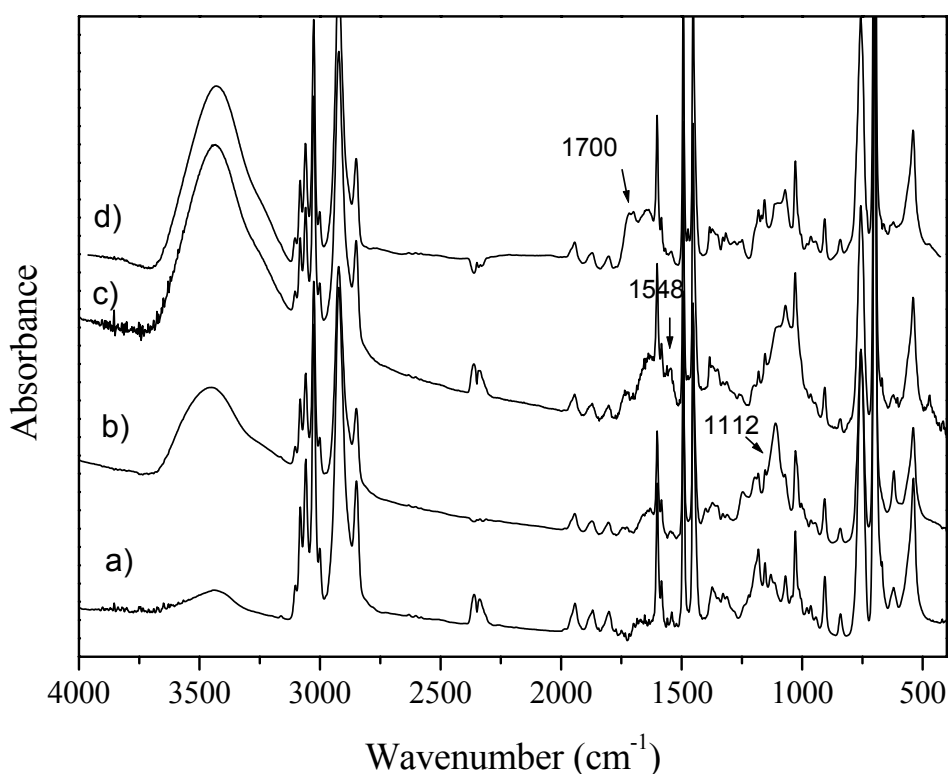


Figure S3. FTIR spectra of a) polystyrene latex, b) polystyrene latex with $\text{PS}_{40}\text{-}b\text{-P(PEGMA1100)}_{70}$ as stabiliser, c) polystyrene latex after the extension with PNaMA, and d) polystyrene latex after the extension with PNaMA and after neutralization.

Table S1. Static (θ_S), advancing (θ_A) and receding (θ_R) contact angles of water obtained by needle-syringe on film samples after annealing at 130 °C for 24 h.

| Film | θ_S | θ_A | θ_R | Ref. |
|---|------------|------------|------------|------------|
| PS latex with SDBS | 92.5 | 109 ± 0.9 | 77.6 ± 1 | 1 |
| PS latex with PS ₄₀ - <i>b</i> -P(PEGMA1100) ₇₀ (3.2 wt%) | 77.7 | 88.2 ± 0.4 | 58.1 ± 1.2 | 1 |
| PS latex with PS ₄₀ - <i>b</i> -P(PEGMA1100) ₇₀ - <i>b</i> -PDMAEMA | 58.7 | 68.5 ± 0.6 | 34.2 ± 2.4 | This study |
| PS latex with PS ₄₀ - <i>b</i> -P(PEGMA1100) ₇₀ - <i>b</i> -PNaMA | 73.8 | 78.5 ± 0.4 | 35.5 ± 1.4 | This study |

References

1. A. Muñoz-Bonilla, A. M. van Herk, J. P. A. Heuts, *Macromolecules*, 2010, **43**, 2721.