Supplementary Information

Photoinduced micellization of block copolymers bearing 4,5-dimethoxy-2-nitrobenzyl side groups

Olivier Bertrand,[a§] Jean-Marc Schumers,[a§] Chandrasekar Kuppan,[a] Jacqueline Marchand-Brynaert,[b] Charles-André Fustin[a*] and Jean-François Gohy[a*]

Experimental

Materials and methods

Styrene (Aldrich, 99 %) and tert-butyl acrylate (tBA, Acros, 99 %) were passed through activated basic alumina (Acros) columns prior to use. Copper bromide (CuBr, Aldrich, 99.999 %), ethyl 2- bromoisobutyrate (EBiB, Acros, 98 %), anisole (Acros. 99 %), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA, Fluka, 97 %), trifluoroacetic acid (TFA, Acros, 99 %) and all the other chemicals were used as received.

Typical procedure for the synthesis of PtBA (PtBA$_{31}$, Entry 1, Table 1).

Under argon, a round-bottom flask, with a stopcock, containing CuBr (82 mg; 0.57 mmol; 1 equiv.) was filled with a solution containing tert-butyl acrylate (tBA; 9.97 mL; 68.68 mmol; 120 equiv.), EBiB (112 mg; 0.57 mmol, 1 equiv.), PMDETA (109 mg; 0.62 mmol; 1.1 equiv.), and anisole (5.90 mL; 40 wt-%) previously degassed by three freeze-pump-thaw cycles. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 90°C for 30 min (tBA conversion = 26 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH_2Cl_2 and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was precipitated in MeOH:H_2O 50:50, filtered and dried in vacuo at 30°C for 24 h, affording a white solid (1.67 g, 70%).

M_n (SEC) = 7,100 g/mol; PDI (SEC) =1.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.1 (m, 3H, CH_2-O, CH-Br), 2.3- 2.0 (b, 73 H, CH backbone), 1.9-1.3 (s, 814H, CH_2 backbone, CH_3 t-Butyl). M_n (NMR) = 4,000 g/mol.

Typical procedure for the synthesis of PtBA-*b*-PS (PtBA$_{31}$-*b*-PS$_{158}$, Entry 2, Table 2).

Under argon, a round bottom flask, with a stopcock, containing CuBr (12 mg; 0.08 mmol; 1 equiv.) was filled with a solution containing PtBA$_{31}$-Br (332 mg; 0.08 mmol, 1 equiv.), styrene (2.61 g; 25.10 mmol; 300 equiv.), PMDETA (16 mg; 0.09 mmol; 1.1 equiv.) and anisole (784 mg; 30 wt-%) previously degassed by three freeze-pump-thaw cycles. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 100°C for 4 h (styrene conversion = 37 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH_2Cl_2 and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was precipitated in hexane, filtered and dried in vacuo at 30°C for 24 h, affording a white powder (1.04 g, 81 %).

M_n (SEC) = 21,000 g/mol; PDI (SEC) =1.14. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-6.30 (b, 250H, HAr; PS), 4.1 (m, 2H, CH_2-O; Chain end), 2.3- 1.1 (b, 1038H, CH backbone, CH_2 backbone, CH_3 t-Butyl). M_n (NMR) = 21,500 g/mol.

Typical procedure for the hydrolysis of PtBA-polymers with TFA/CH_2Cl_2 (PAA$_{31}$-*b*-PS$_{168}$, Entry 2, Table 3).

In a round bottom flask, PtBA$_{31}$-*b*-PS$_{168}$ (974 mg; 1.40 mmol in tBA units; 1 equiv.) was dissolved in dichloromethane (97.4 mL, 0.01 M). TFA (1.46 mL, 19.72 mmol, 14 equiv.) was added and the solution was stirred at 20°C for 24 h. The solvent was removed under reduced pressure and the residue was kept in a minimum amount of DMF and dialyzed against methanol. The polymer was precipitated in hexane, filtered and dried in vacuo at 30°C for 24 h, affording a white powder (813 mg, 91%).

^{1}H NMR (300 MHz, DMF-d$_7$): δ 7.3-6.1 (b, 250H, HAr; PS), 2.2 (b, 74H, CH backbone PAA), 2.1- 1.1 (b, 300H, CH_2 backbone PAA + PS). M_n (NMR) = 19,700 g/mol.

Typical procedure for the photocleavage in solution (UV-Vis)

A solution of PDMNBA$_{43}$-*b*-PS$_{49}$ in $CHCl_3$ (C= 20 mg/L) was irradiated under stirring at 350 nm. The photocleavage was followed by UV-visible spectroscopy until no change was observed in the shape of the spectrograms (t(min)= 0, 5, 10, 15, 20, 25, 30, 40, 45).

Typical procedure for determination of the quenching effect of dimethoxynitrosobenzaldehyde

A solution of PDMNBA$_{43}$-*b*-PS$_{49}$ (C= 0.1 g/L) in $CHCl_3$ stabilized with EtOH was irradiated at 350 nm. After 60 min irradiation time, coumarin 343 was added to the medium (C= 0.3 mg/L). The mixture was stirred for 15 min and analyzed by fluorescence spectroscopy.

Typical procedure for encapsulation of the dye into the micellar core by direct dissolution

PAA$_{43}$-*b*-PS$_{49}$ (C= 0.1 g/L) was added to a solution of coumarin 343 (C= 0.3 mg/L) in $CHCl_3$ stabilized with EtOH. The mixture was stirred and the encapsulation was followed by fluorescence spectroscopy (t (h)= 0, 1, 20).

Typical procedure for diffusion of the dye into the micellar core

A quartz cell was filled with a solution of PAA$_{43}$-*b*-PS$_{49}$ micelles (C= 0.1 g/L) and with Coumarin 343 (C= 0.3 mg/L) in $CHCl_3$ stabilized with EtOH. The solution was stirred and the diffusion of the dye into the micellar core was followed by fluorescence spectroscopy (t (min)= 0, 10, 20, 30, 40, 50, 60).

Additional comments on the synthesis

As mention in the paper core, the photocleavable polymers are obtained by the grafting of the desired *o*-nitrobenzyl derivative onto PAA-*b*-PS precursors. The latter are synthesized in three steps: i) polymerization of *tert*-butyl acrylate by ATRP, ii) copolymerization of styrene by ATRP from the PtBA macroinitiator to obtain PtBA-*b*-PS copolymers, iii) hydrolysis of the *tert*-butyl esters of the PtBA block.

Table 1 presents the results obtained for the polymerization of *tert*-butyl acrylate (tBA) by ATRP. The polymerizations were conducted in anisole at 80°C or 90°C using CuBr/PMDETA as catalytic system in conjunction with EBiB as initiator.[1] Well-defined PtBA's with molar masses ranging from 4,000 to 19,000 g/mol (M_n, NMR) and with narrow molar mass distributions (PDI's < 1.25) were obtained.

Table 1: Experimental conditions and obtained results for the ATRP of PtBA.

Entry[a]	PtBA[b]	t[c] (h)	conv[d] (%)	M_n (RMN)[e] (g/mol)	M_n (SEC)[f] (g/mol)	PDI[f]
1	PtBA$_{31}$	0.5	26	4,000	7,100	1.22
2	PtBA$_{43}$	1	33	5,700	7,100	1.20
3	PtBA$_{112}$	2.5	76	14,400	16,000	1.10

[a] Reaction conditions: [EBiB]/[CuBr]/[PMEDTA] = 1/1/1.1, anisole 40 wt%, T = 90°C. [b] The numbers in subscript are the average degrees of polymerization determined by ^{1}H NMR. [c] t = reaction time. [d] conv = conversion of monomer. [e] Molar mass of the polymer determined by ^{1}H NMR. [f] M_n and PDIs were determined by SEC using a PS calibration.

The next step consisted in polymerizing styrene with the synthesized PtBA macroinitiators in order to yield PtBA-*b*-PS block copolymers. The reaction conditions and the results for those copolymerizations are shown in **Table 2**. Similar reaction conditions than those used for the polymerizations of tBA were investigated and several well-defined PtBA-*b*-PS's with molar masses ranging from 10,600 to 27,500 g/mol (M_n, NMR) and with PDI's lower than 1.25 were successfully synthesized.

After the synthesis of PtBA-*b*-PS copolymers, the hydrolysis of the *t*-butyl esters into carboxylic acid functions has been performed in acidic conditions. The polymers were stirred in dichloromethane with trifluoroacetic acid as described in the literature.[2] The starting PtBA-*b*-PS and the corresponding PAA-*b*-PS obtained by hydrolysis are presented in **Table 3**.

Table 3: Hydrolysis of the *tert*-butyl side groups of the PtBA sequence.

Entry[a]	PtBA-*b*-PS	PAA-*b*-PS	e_h[b] (%)
1	PtBA$_{43}$-*b*-PS$_{49}$	PAA$_{43}$-*b*-PS$_{49}$	96
2	PtBA$_{31}$-*b*-PS$_{168}$	PAA$_{31}$-*b*-PS$_{168}$	95
3	PtBA$_{112}$-*b*-PS$_{125}$	PAA$_{112}$-*b*-PS$_{125}$	95

[a] Reaction conditions: $C_{polymer}$ = 10 g/L, TFA = 10 eq. compared to tBA, 20°C, 48 h. [b] e_h = hydrolysis yield determined by ^{1}H NMR.

Table 2: Experimental conditions and obtained results for the copolymerization of styrene with a PtBA macroinitiator.

Entry[a]	PtBA-*b*-PS[b]	styrene (eq.)	anisole (wt%)	t[c] (h)	conv[d] (%)	M_n (RMN)[e] (g/mol)	M_n (SEC)[f] (g/mol)	PDI[f]
1	PtBA$_{43}$-*b*-PS$_{49}$	200	65	1.25	32	10,600	11,600	1.15
2	PtBA$_{31}$-*b*-PS$_{168}$	300	60	4	37	21,500	21,000	1.14
3	PtBA$_{112}$-*b*-PS$_{125}$	300	60	2.5	33	27,500	21,600	1.21

[a] Reaction conditions: [PtBA]/[CuBr]/[PMEDTA] = 1/1/1.1, T = 100°C. [b] The numbers in subscript are the average degrees of polymerization determined from ^{1}H NMR. [C] t = reaction time. [d] conv = conversion of monomer. [e] Molar mass of the polymer determined by ^{1}H NMR. [f] M_n and PDIs were determined by SEC using a PS calibration. [g] $r_{100\%}$ = mass fraction of the future PDMNBA block at 100% functionalization.

Notes and references

[a] *Institute of Condensed Matter and Nanosciences* (IMCN), *Bio- and Soft matter* (BSMA), *Université catholique de Louvain, Place L. Pasteur 1, Louvain-la-Neuve, Belgium; E-mail:charles-andre.fustin@uclouvain.be, jean-francois.gohy@uclouvain.be*
[b] *Institute of Condensed Matter and Nanosciences* (IMCN), *Molecules, Solids and Reactivity* (MOST), *Université catholique de Louvain, Place L. Pasteur 1, Louvain-la-Neuve, Belgium;*

§These authors contributed equally to the present work

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