Supporting Information

Mechanistic insight into surface-initiated polymerization of methyl methacrylate and styrene via ATRP from ordered mesoporous silica particles.

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Preparation of ordered mesoporous silica particles.

Preparation of MSU-P123.[1] Distilled water (500 mL) and Pluronic P123 (7.5 g) were mixed together before adding 420 µL of hydrochloric acid 12 M to reach a pH value lower than 2. The mixture was stirred during 1 h at room temperature until complete dissolution of the Pluronic surfactant. TEOS (33.3 g) was transferred into the solution and the white emulsion was stirred during 6 h until complete hydrolysis of TEOS (homogeneous solution). Ammonium fluoride (11 mL) was added in order to catalyze the silica condensation and the formation of a precipitate was then observed. Silica was filtered, washed with 250 mL of ethanol, dried at 130 °C during 6 hours and finally calcined at 600 °C.

Preparation of MSU-Brij.[1] The Brij 56 surfactant (11 g) was mixed with 750 mL of acidic water (pH 2). After complete homogenization, 19.6 g of TEOS were added and the solution was stirred during 4 H 30 min at ambient temperature and 30 min at 45 °C. The aqueous solution of NaF catalyst (51 mL, 0.25 M, NaF / TEOS = 0.1) was introduced and the condensation reaction was carried out overnight at 45 °C. The silica particles were filtered and washed with ethanol before being dried at 110 °C during 1 h. Silica particles were subsequently calcined at 200 °C during 6 h followed by 6 h at 600 °C. The recovered ordered mesoporous silica particles displayed ordered mesopores with an average diameter of 14 nm, higher than expected with the Brij 56 surfactant used as template. This was probably due to the collapse of silica walls. The volume fraction of each mesopore population was as follows: 7 v-% of 5 nm-diameter mesopores and 93 v-% of 14 nm-diameter mesopores. The surface of the largest pores corresponded to 80 % of the total surface.

Preparation of SBA-15.[2] The amphiphilic copolymer (Pluronic P123) was dissolved in water at 40°C during several hours before adding hydrochloric acid and TEOS. The mixture was stirred 24 hours at 40°C in a closed bottle (precipitation of silica) before heating the bottle at 120°C in a oven during 24 hours. The recovered silica was filtered, washed and calcined at 600°C.

Preparation of MCM-41.[3] A mixture containing 24 g of CTAB, 32.2 g of TEOS and 500 mL of ethanol was stirred to recover a homogeneous solution before adding the aqueous ammonia solution (130 mL of 28 v-% ammonia solution diluted in 400 mL of distilled water). The mixture was stirred at room temperature during 1 h. The silica suspension was filtered and washed with 250 mL of ethanol to remove the majority of CTAB surfactant. Silica was dried at 130 °C during several hours and subsequently calcined at 600 °C in the oven.

Preparation of spherical silica nanoparticles (SN) via the Stöber technique

The spherical silica particles (SN-1) were synthesized according to the Stöber process widely described in the literature.[4,5] To a solution containing 1 L of ethanol, 80 mL of deionized water, 40 mL of ammonia solution (28 – 30 %) were added 56 g of TEOS. The solution was stirred overnight at room temperature. A suspension of spherical silica particles was obtained. This crude suspension was directly used for the synthesis of CSSN nanoparticles. The average

particle diameter measured from TEM pictures was 270 nm (SN-1). The TEOS : NH_3 : EtOH : H_2O : molar ratio was 1 : 2.3 : 64 : 22.

For the synthesis of the dense spherical cores (SN-2, stöber silica particles), a solution was prepared with ethanol (1L, 17.13 mol), H_2O (80 mL, 4.44 mol), and 40 mL of NH_3 28-30% in a 2 L conical flask. It was stirred during 30 min then 60 mL of TEOS (0.268 mol) were slowly added. After a while the colorless solution became cloudy and it was left stirring at room temperature overnight.

Synthesis of the core-shell spherical nanoparticles with ordered mesoporous shell and dense silica core (CSSN-30 and CSSN-105)

For the synthesis of the 30 nm thickness mesoporous shell (CSSN-30), 300 mL of the SN-2 solution were taken and transferred into another conical flask, where 335 mL of H_2O and 47.4 mL of a 0.11 M CTAB solution (5.21×10^{-3} mol) were added. The suspension was stirred during 30 min then 3.17 mL of TEOS (0.015 mol) were added. After stirring overnight at room temperature, the suspension was centrifuged at 7000 rpm for 15 min and the recovered silica was calcined in an oven during 18 hours at 500°C.

For the synthesis of the 105 nm thickness mesoporous shell (CSSN-105), 150 mL of the SN-2 solution were transferred into a conical flask and the following reagents were added: 228 mL of ethanol, 825 mL of H_2O, 8.5 mL of NH_3 solution 28-30%, and 121 mL of 0.11 M CTAB solution (0.013 mol). The suspension was stirred during 1 hour then 8.68 mL of TEOS (0.039 mol) were added and the reaction was carried out at room temperature overnight. Silica particles were recovered after centrifugation (7000 rpm, 15 min) and calcination (500°C, 18 h).

Synthesis of the silylated alkyl bromide initiator

General procedure for esterification step

In a round bottom flask were introduced 10 g of hexen-1-ol (9.9×10^{-2} mol), 14 g of dry triethylamine (1.4×10^{-1} mol) and 44 g of dry toluene. The mixture was cooled at 0°C before adding dropwise 15 mL of 2-bromoisobutyryl bromide (1.2×10^{-1} mol). The mixture was stirred 1 h at 0°C and 4 h at room temperature. The precipitated triethylamine hydrochloride was removed by filtration, and the solution was washed twice with 50 mL of water and three times with 50 mL of sodium hydrogenocarbonate solution. The organic phase containing pent-4-enyl-2-bromoisobutyrate **(1)** was recovered, dried with $MgSO_4$ and toluene was

subsequently evaporated under vacuum. A similar procedure was used for the synthesis of pent-4-enyl-2-bromopropionate **(2).**

Pent-4-enyl-2-bromoisobutyrate **(1)**. Yield 87%; ^{1}H NMR ($CDCl_3$): δ = 1.54 (quintet, CH_2), 1.75 (quintet, CH_2), 1.93 (s, 2 CH_3), 2.19 (quartet, CH_2), 4.23 (t, CH_2), 5.06 (m, alkene, CH_2), and 5.85 (complex m, alkene, C*H*).

Pent-4-enyl-2-bromopropionate **(2)**. Yield 87%; ^{1}H NMR ($CDCl_3$): δ = 1.54 (quintet, CH_2), 1.75 (quintet, CH_2), 1.89 (d, CH_3), 2.19 (quartet, CH_2), 4.23 (t, CH_2), 4.34 (q, C*H*), 5.06 (m, 2H, alkene, CH_2), and 5.85 (complex m, 1H, alkene,C*H*).

General procedure for hydrosilylation step

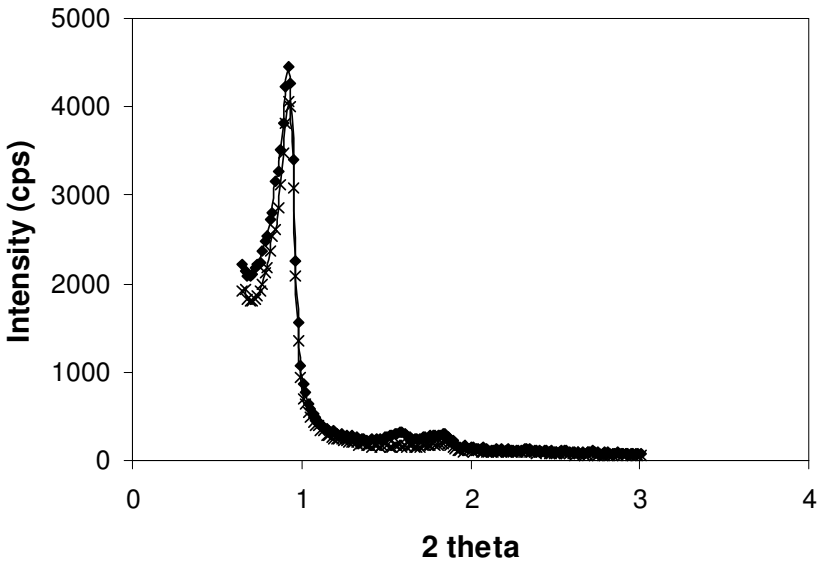
The solution of alkene containing 8 g of pent-4-enyl-2-bromoisobutyrate (3.2×10^{-2} mol) and 35.8 mL of dimethylchlorosilane (3.2×10^{-1} mol) was prepared under nitrogen atmosphere and subsequently transferred under nitrogen via an double-tipped needle into a round bottom flask containing 85 mg of dihydrogen hexachloroplatinate hexahydrate (1.6×10^{-4} mol). The solution was stirred 16 h at room temperature. After adding 20 mL of dry dichloromethane, the excess of dimethylchlorosilane was evaporated under reduced pressure, the crude product was then passed through a short column of dry sodium sulfate to remove the black catalyst, the column was washed with dry dichloromethane (100 mL), and the dichloromethane was removed under reduced pressure. The final product ((6-dimethylchlorosilylhexyl)-2-bromoisobutyrate, **(3)**) was orange and contained only 5 mol-% of dimeric siloxane impurities as observed by proton NMR (^{1}H NMR ($CDCl_3$) δ *(ppm)* 0.02 – 0.08, 12H). The (6-dimethylchlorosilylhexyl)-2-bromopropionate **(4)** was synthesized according to the same procedure.

(6-dimethylchlorosilylhexyl)-2-bromoisobutyrate **(3)**. ^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 2 CH_3), 0.81 (m, CH_2), 1.38 (m, CH_2), 1.67 (m, CH_2), 1.92 (s, 2 CH_3), 4.16 (t, CH_2).

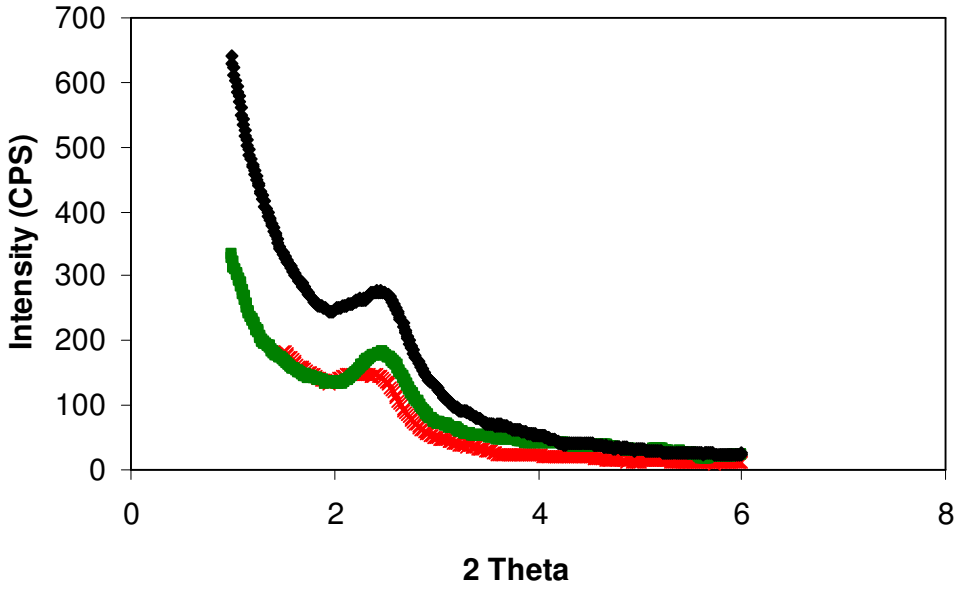
(6-dimethylchlorosilylhexyl)-2-bromopropionate **(4)**. ^{1}H NMR ($CDCl_3$): δ = 0.39 (s, 6H, 2 CH_3), 0.81 (m, 2H, CH_2), 1.38 (m, 6H, CH_2), 1.67 (m, 2H, CH_2), 1.89 (d, CH_3), 4.16 (t, 2H, CH_2), 4.34 (q, C*H*).

Figure SI-1. Overlay of X-Ray diffraction patterns of **(A)** micrometric OMS particles: MSU-P123 (◆); MSU-P123-BiB functionalized with bromoisobutyrate-based initiator (×); **(B)** submicronic spherical OMS particles: CSSN-105 (◆), CSSN-45 (×), CSSN-30 (■).

(A)



(B)



Calculation of the monomer conversion (x) by proton NMR as a function of time (t).

$$x = 1 - \frac{[M]_t}{[M]_0} = 1 - \frac{[M]_t / [DMF]_t}{[M]_0 / [DMF]_0} \text{ because } [DMF]_0 = [DMF]_t$$

Moreover $\frac{[M]_0}{[DMF]_0} = \frac{I_{M_0}}{I_{DMF_0}}$ et $\frac{[M]_t}{[DMF]_t} = \frac{I_{M_t}}{I_{DMF_t}}$ with I_M corresponding to the NMR integration of two vinylic protons of the monomer (protons **(1)** and **(1')**: 2H, *2 s*, 5.5 – 6.5 ppm for MMA (Figure SI-2), and 2H, *2 d*, 5 - 6 ppm for styrene (Figure SI-3)) and I_{DMF} corresponds to the NMR integration of six DMF protons (6H, *d*, 2.8 ppm, protons **(4)**).

Then, the calculation of monomer conversion follows equation (1):

$$\mathbf{x} = 1 - \frac{(\mathbf{I_{M_t}} / 2) / (\mathbf{I_{DMF_t}} / 6)}{(\mathbf{I_{M_0}} / 2) / (\mathbf{I_{DMF_0}} / 6)} \qquad \text{Equation (1)}$$

Figure SI-2. ^{1}H NMR spectrum of the crude solution for the ATRP of methyl methacrylate carried out in toluene in the presence of DMF (absence of free initiator).

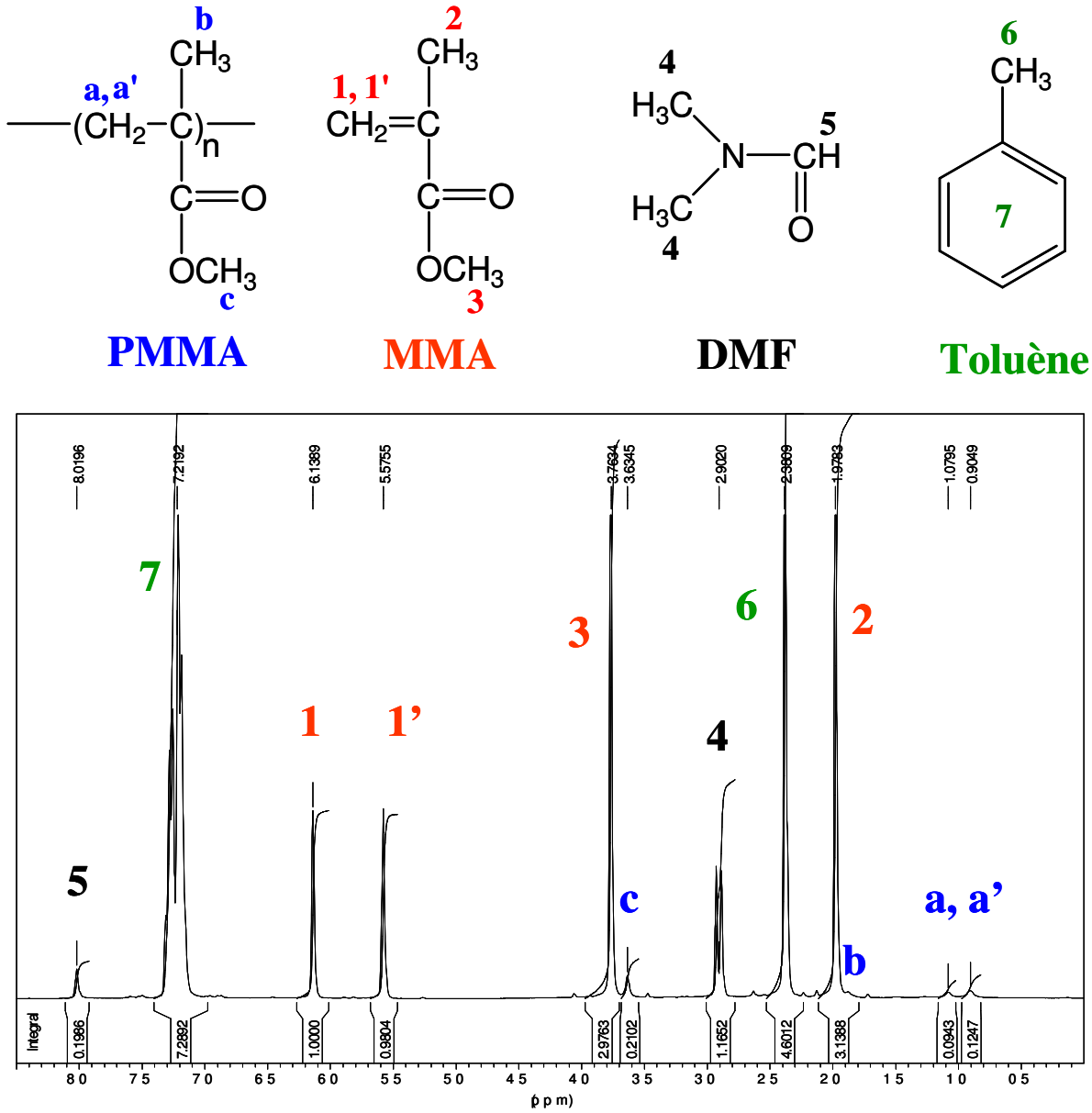


Figure SI-3. ^{1}H NMR spectrum of the crude solution for the ATRP of styrene carried out in bulk in the presence of DMF (absence of free initiator).

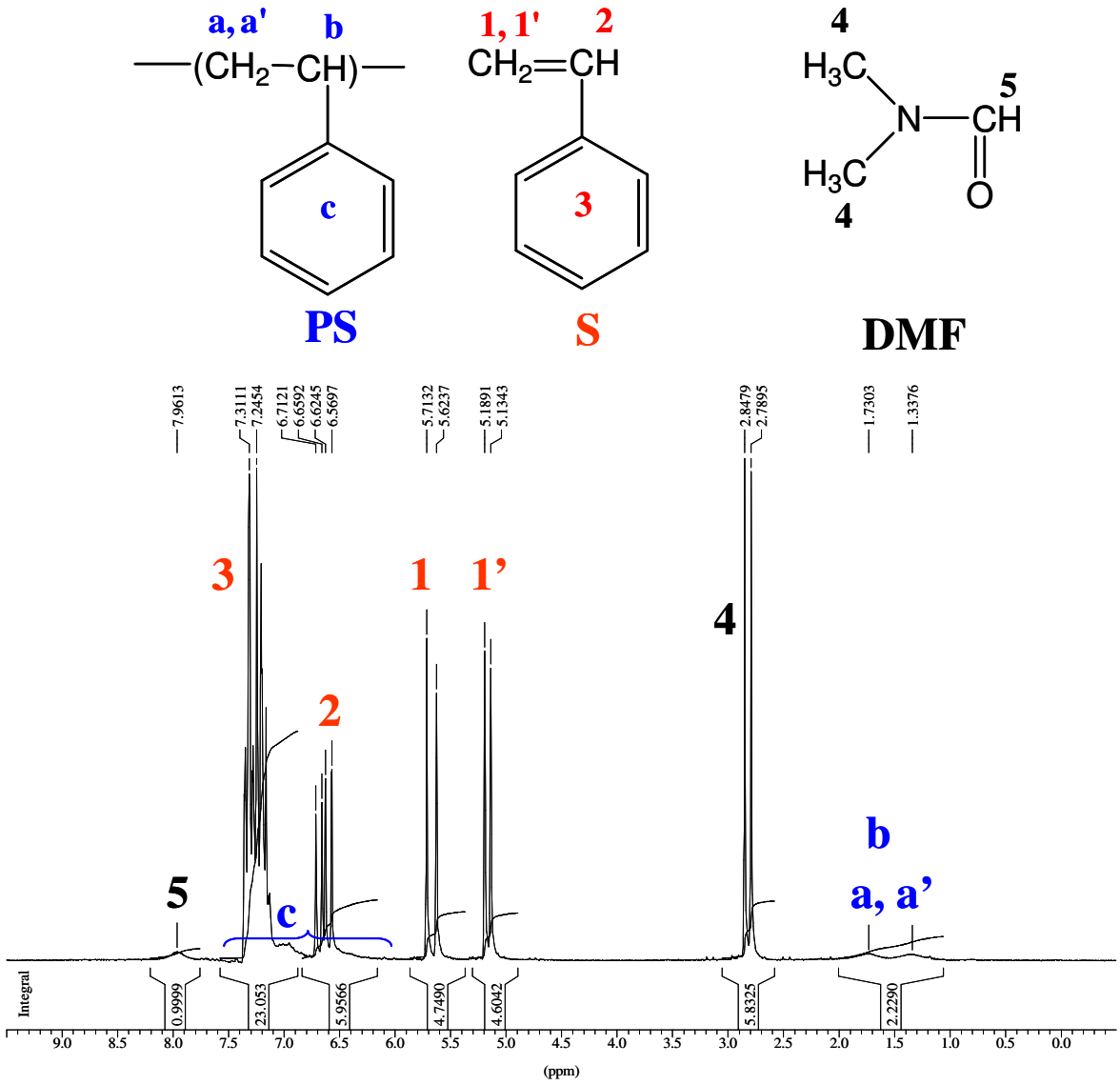


Figure SI-4. Overlay of Infra-Red spectra (IR) of (a) CSSN functionalized with bromoisobutyrate initiator, (b) CSSN functionalized with PMMA (Expt 12 in Table 3).

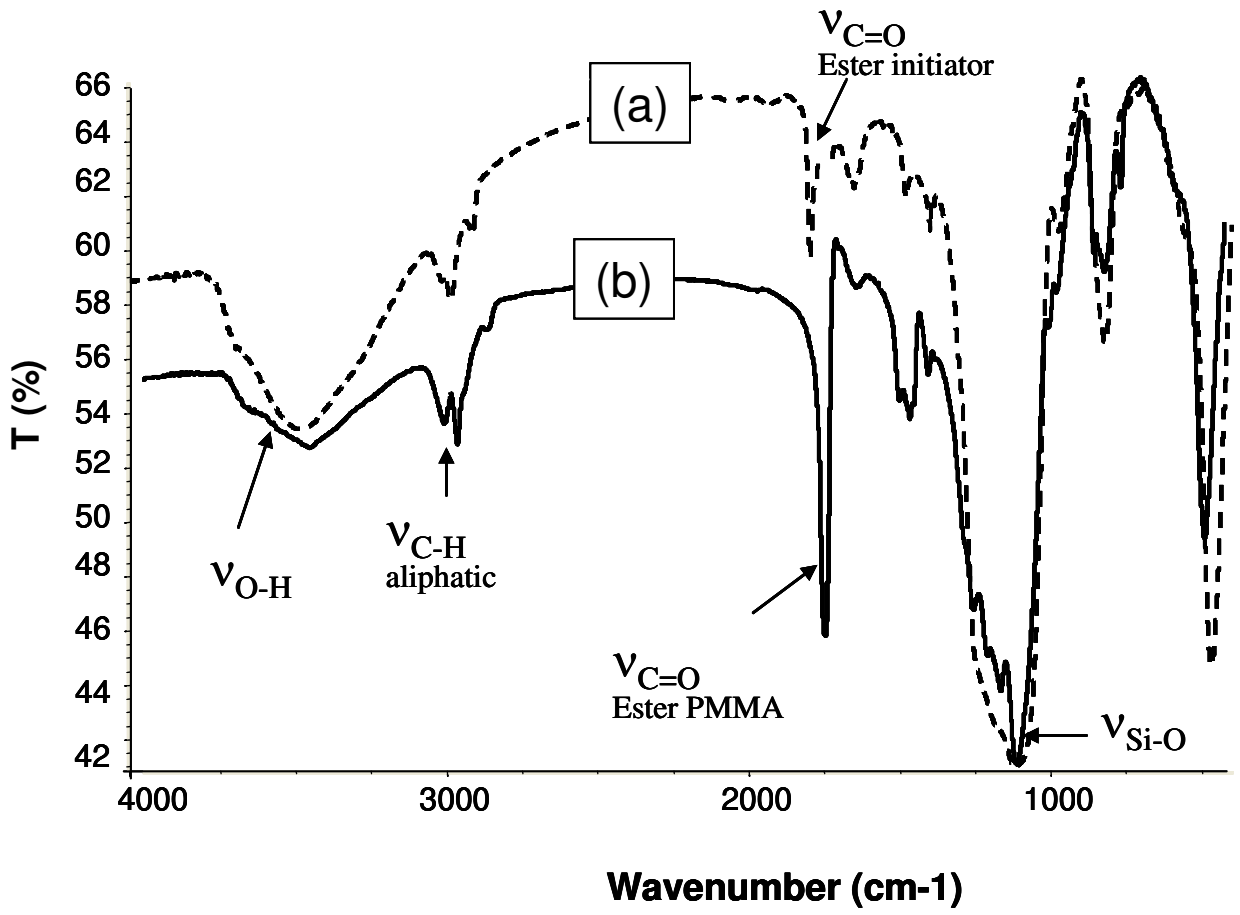


Figure SI-5. SI-ATRP of MMA initiated from either SBA-15-BiB (blue line, expt 3 in table 3) or MSU P123-BiB (black line, expt 4 in Table 3) in the presence of 60 mol-% of free initiator *vs.* grafted initiator: overlay of SEC traces of cleaved PMMA chains. SBA-15 and MSU P123 silica were synthesized in the absence or in the presence of NaF catalyst respectively.

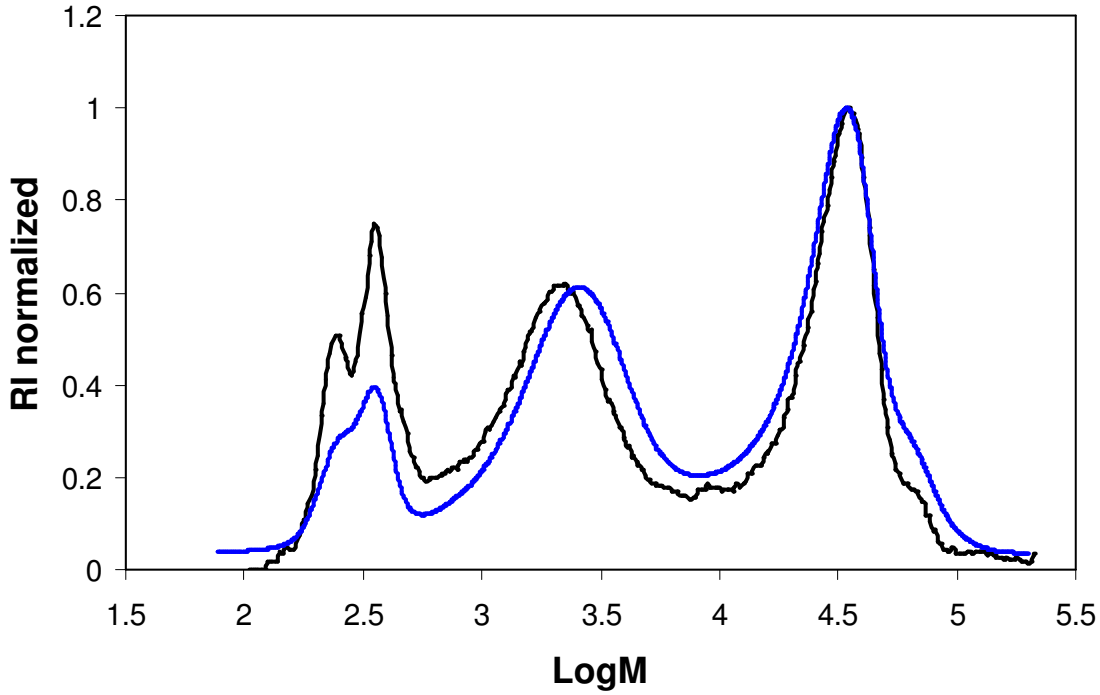


Figure SI-6. SI-ATRP of MMA initiated from MSU P123-BiB in the presence of 60 mol-% of free initiator *vs.* total initiator (free + grafted): overlay of SEC traces of free PMMA chains (dashed line) and cleaved PMMA chains (plain line). Influence of the [Cu]:[Ligand] ratio: **(A)** Expt 2 in Table 3, [Cu]:[HMTETA] = 1:1; **(B)** Expt 2 in Table 3 but using [Cu]:[HMTETA] = 1:0.3.

(A) **(B)**

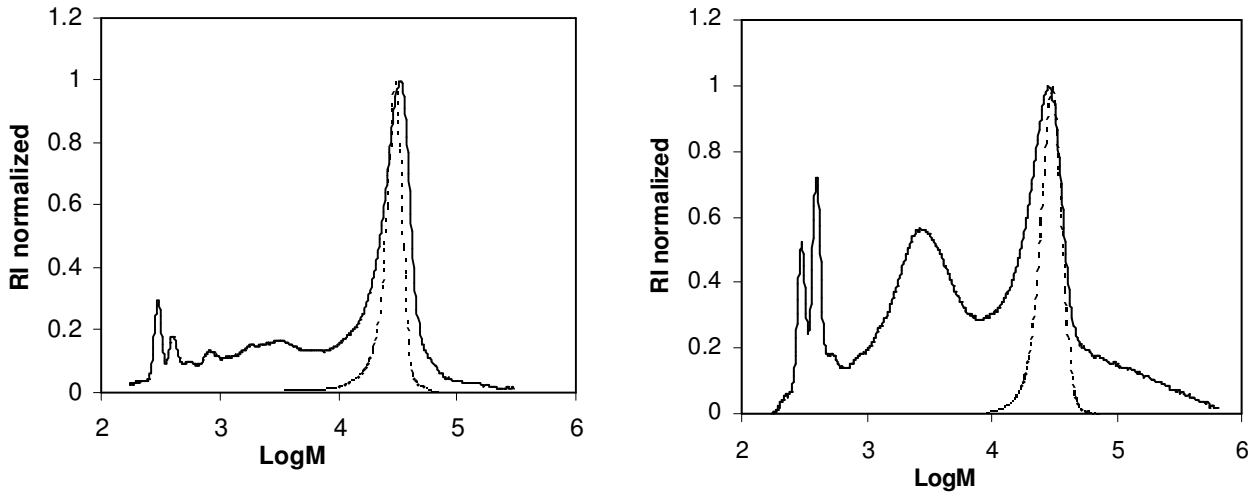
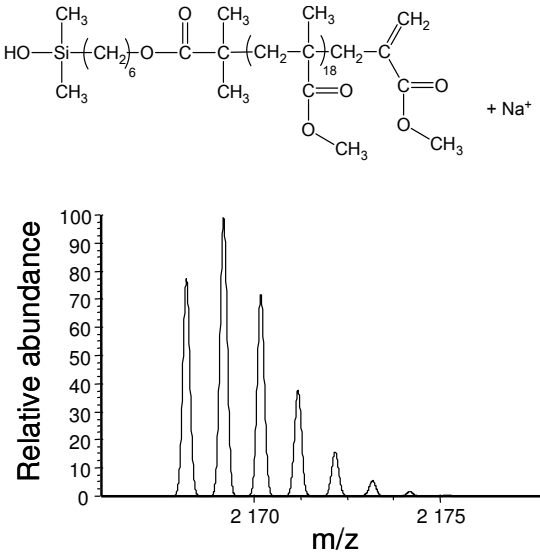
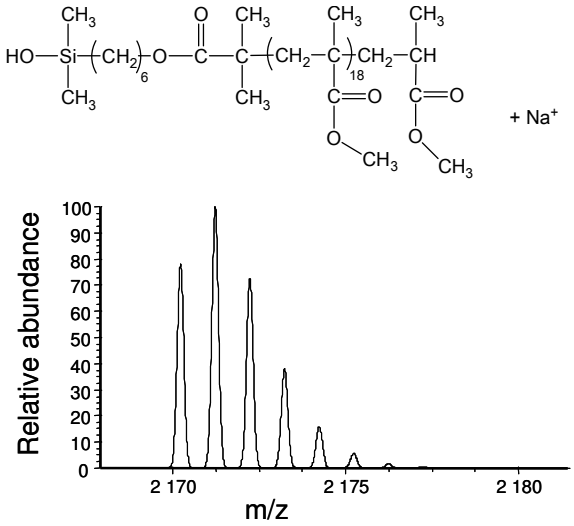


Figure SI-7. Comparison between the **theoretical isotopic distributions** of PMMA chains containing either insaturated chain ends **(a)**, or saturated chain ends **(b)** or a mixture of 50 mol-% of insaturated chain end and 50 mol-% of saturated chain end **(c)** on one hand and the **experimental MALDI-TOF isotopic distribution** of the cleaved PMMA chains **(d)** on the other hand.

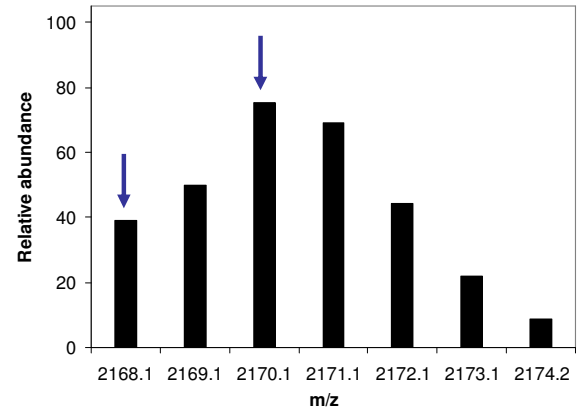
(a)



(b)



(c)



(d)

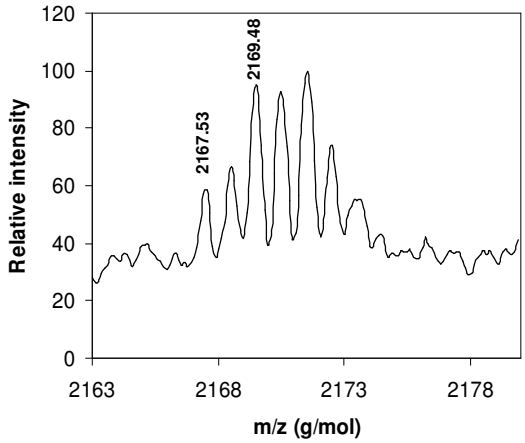
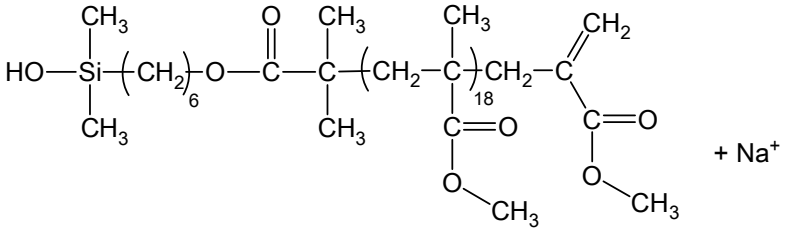
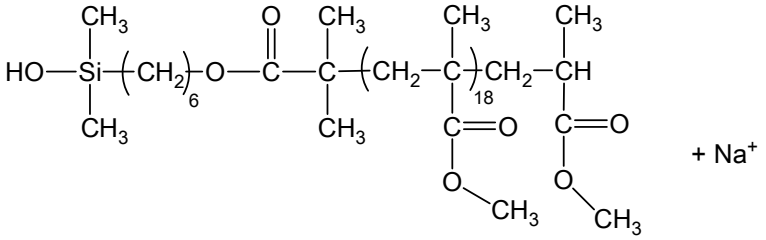
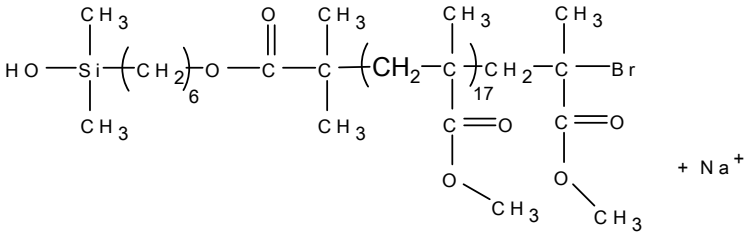


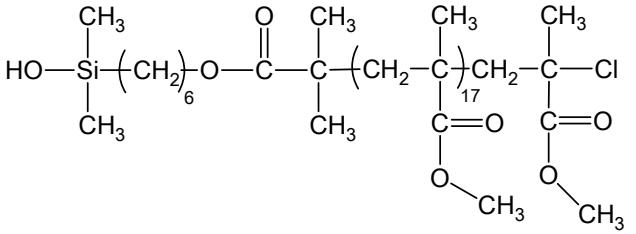
Figure SI-8. Theoretical molar masses of the possible macromolecular structures for the cleaved PMMA chains (fraction of low M_n). The MALDI-TOF analysis was performed in reflector mode.

Lower atomic mass of the isotope (g.mol^{-1})						
O	**Br**	**Cl**	**Si**	**C**	**H**	**Na**
15.994915	78.918336	34.97	27.9769	12.00	1.007825	22.98977

Possible macromolecular structure	**Theoretical mass** (g.mol^{-1})
	**2168.13541**
	**2170.15106**



2148.00914



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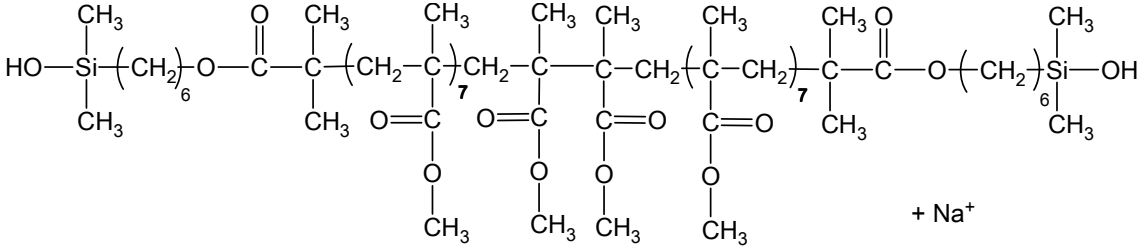
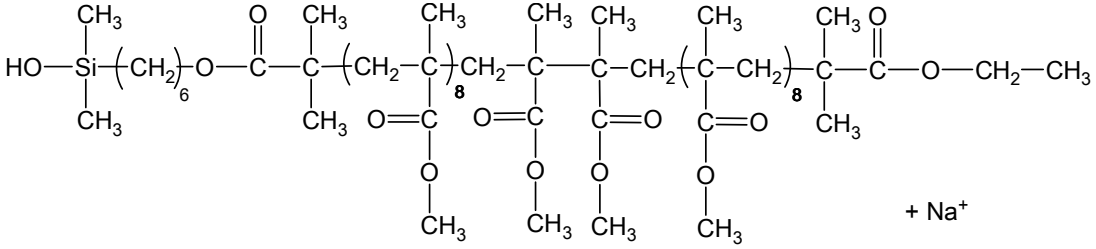


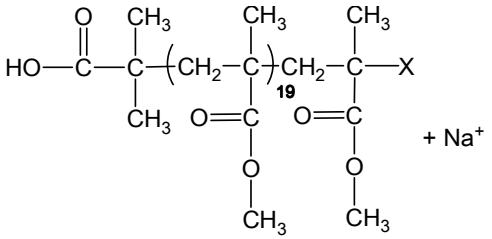
2114.14325

(termination reactions by combination between two grafted PMMA chains)



2184.16671

(termination reactions by combination between free and grafted PMMA chains)



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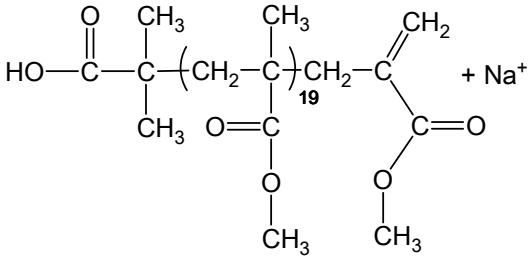
X = Br : M = 2190.00131

X = H : M = 2112.0908



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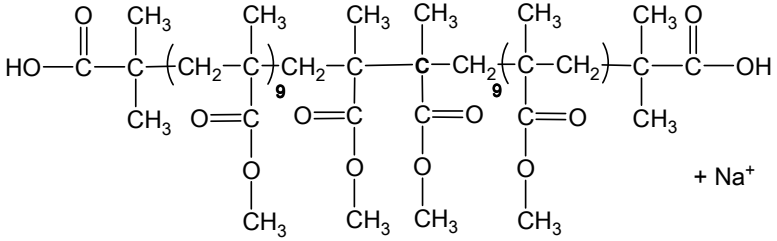

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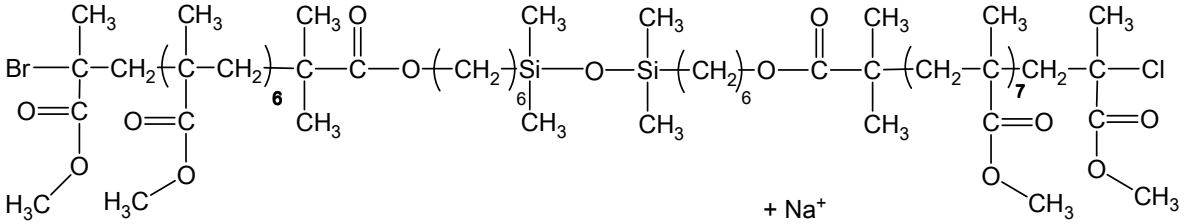

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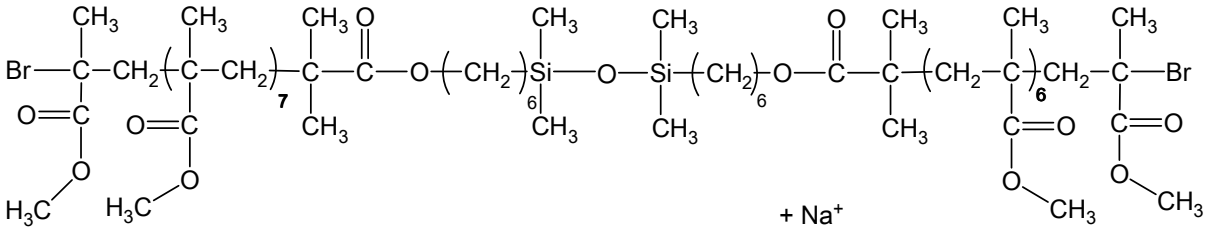

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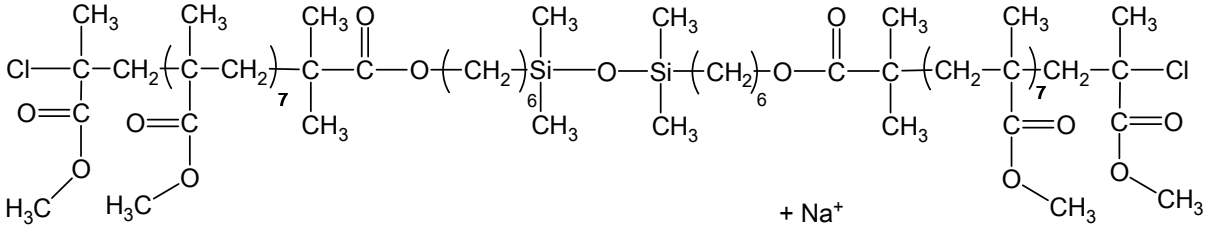

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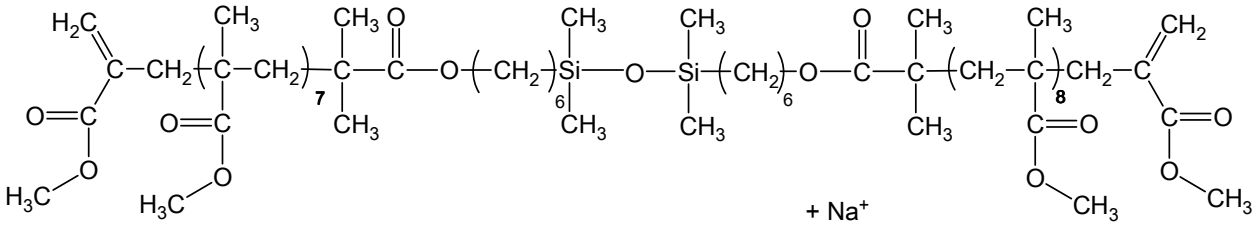

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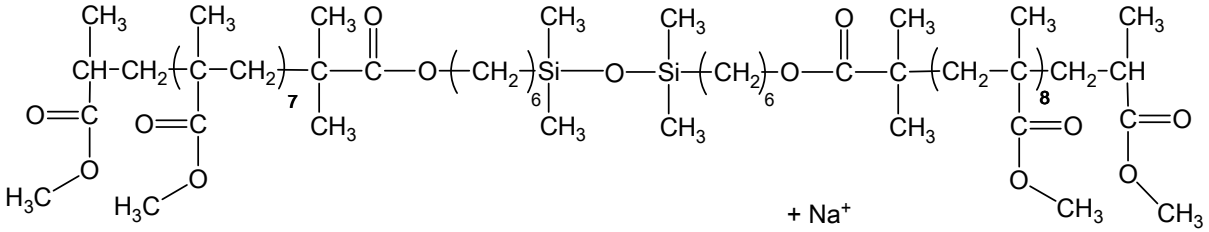

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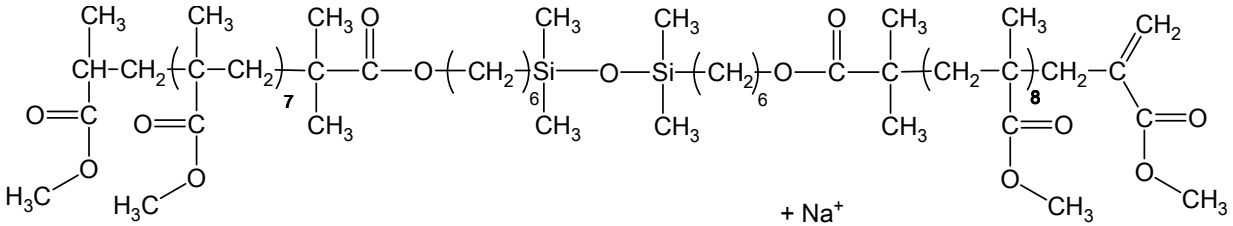

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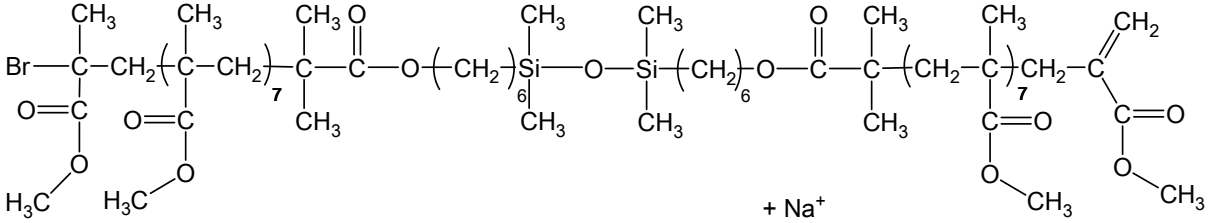

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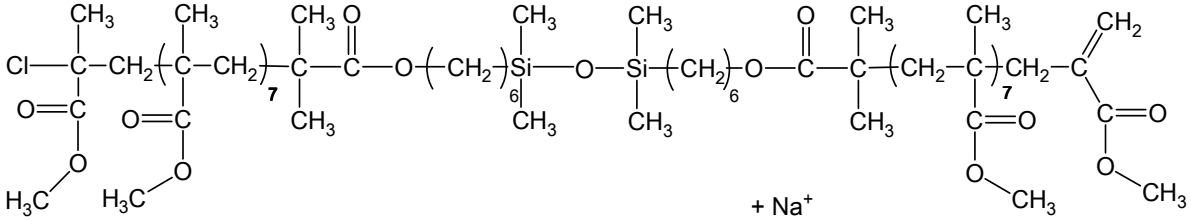

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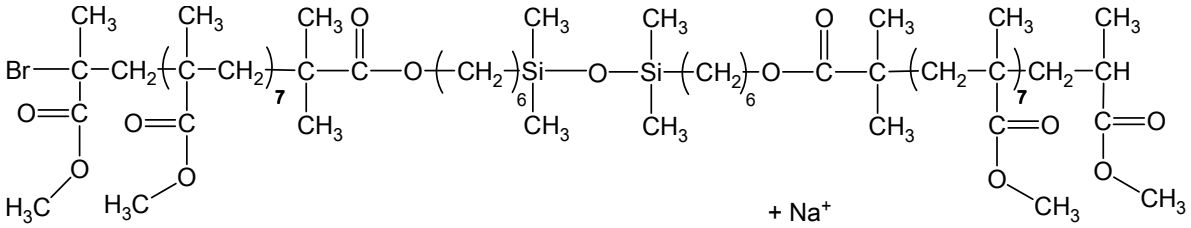

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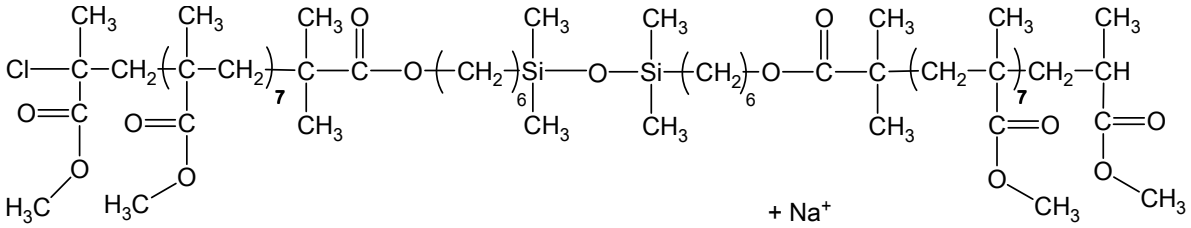

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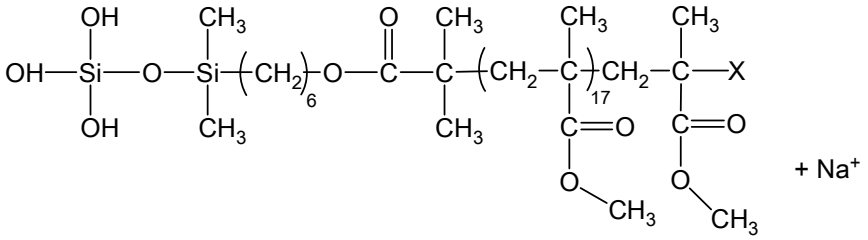

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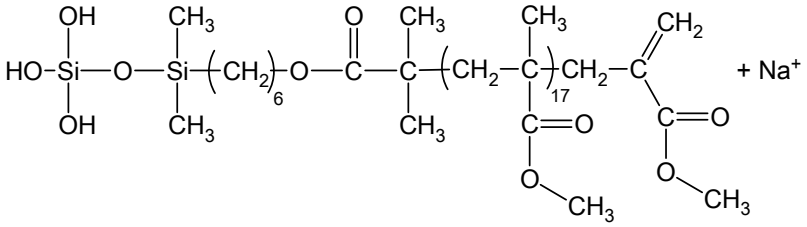
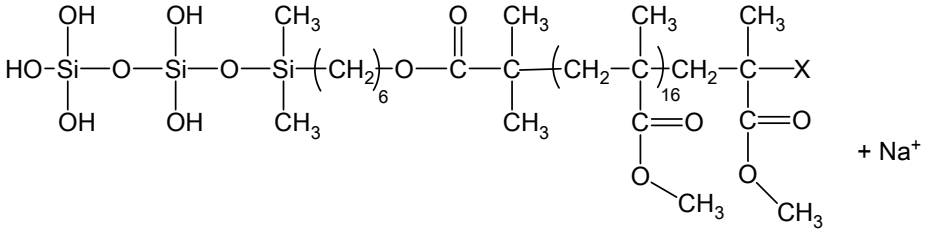
X = Br : M = 2225.98641

X = H : M = 2148.0759

(Presence of oligomeric silica-based chain end)



2146.06025

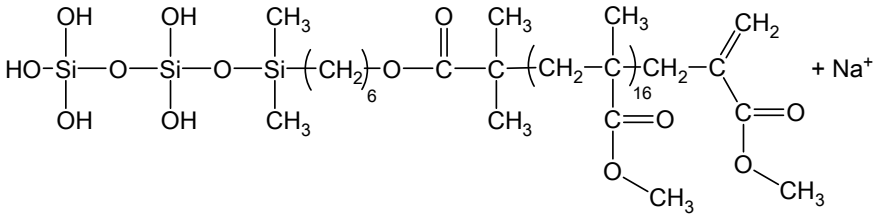


X = Cl : M = **2159.96294**

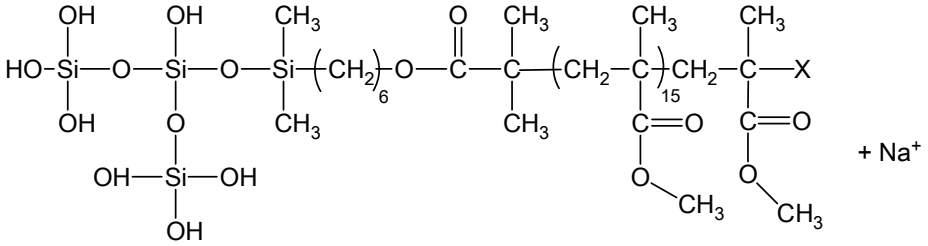
X = Br : M = 2203.91128

X = H : M = 2126.00077

(Presence of oligomeric silica-based chain end)



2123.98512

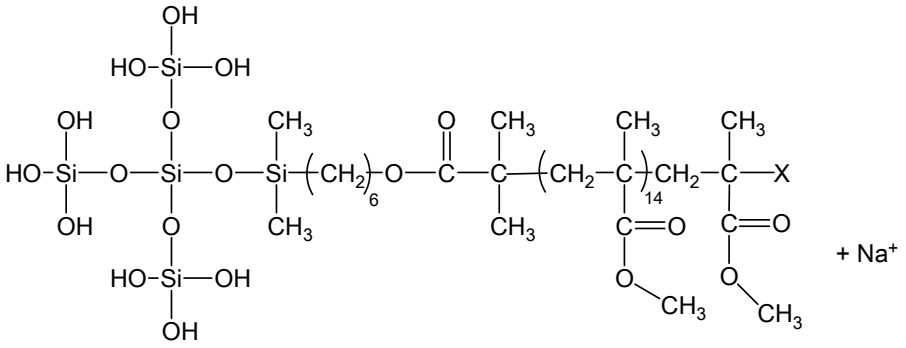


X = Cl : M = 2137.89563

X = Br : M = 2181.84397

X = H : M = 2103.93346

(Presence of oligomeric silica-based chain end)



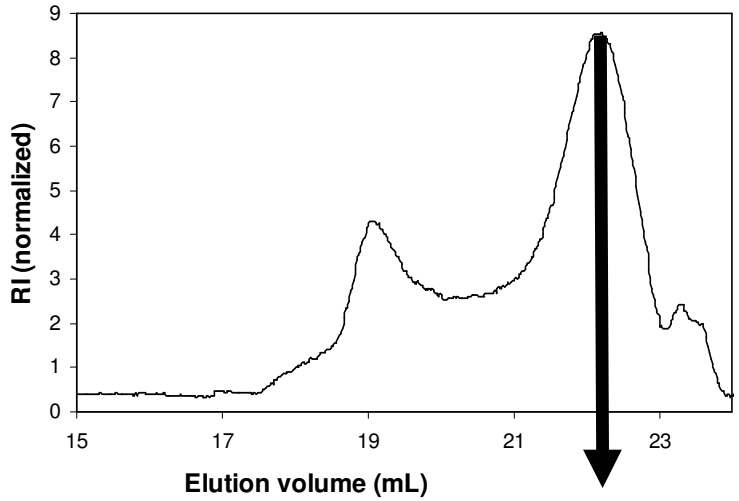
X = Cl : M = 2115.82832

X = Br : M = **2159.77666**

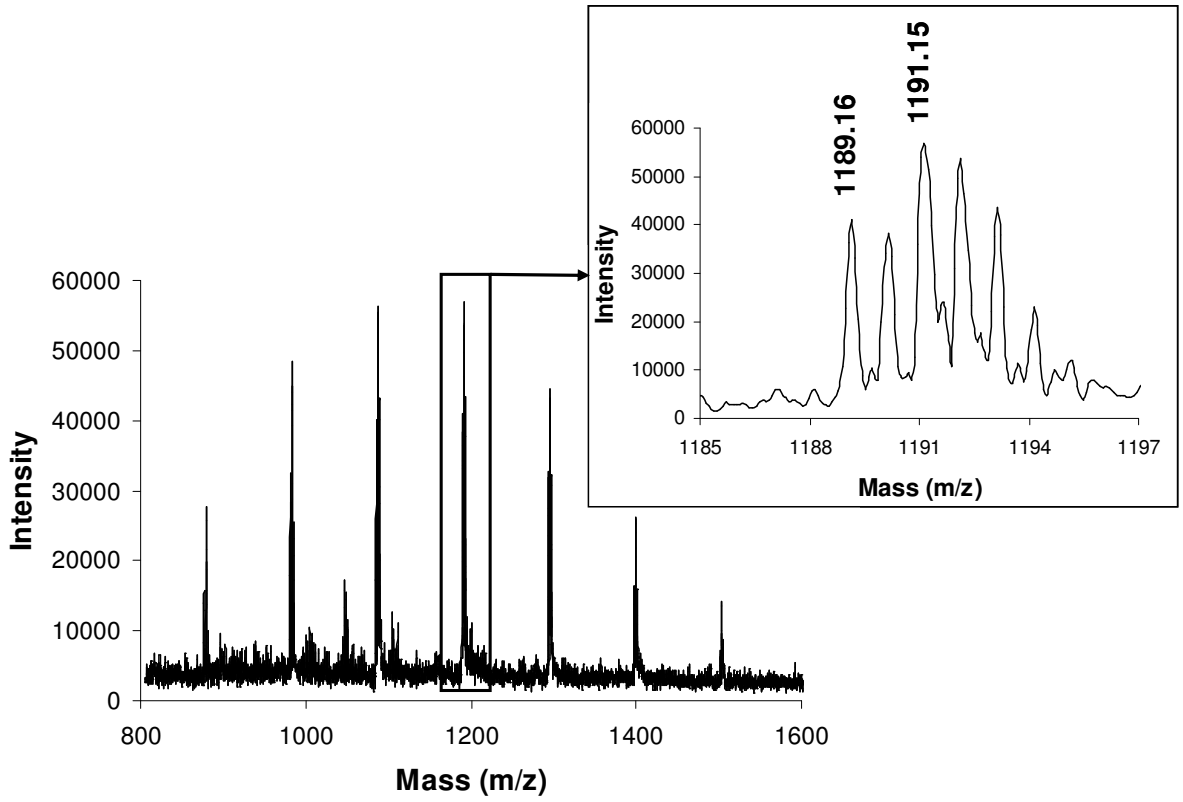
X = H : M = 2181.918575

(Presence of oligomeric silica-based chain end)

Figure SI-9. Analysis of the cleaved PS chains after SI-ATRP of styrene initiated from the micrometric MSU-Brij-BP OMS particles (Expt 17 in Table 4): SEC chromatogram and MALDI-TOF spectra (reflector mode) of the low M_n fraction recovered after fractionation by semi-preparative SEC. Theoretical molar masses of the cleaved PS chains corresponds to the monoisotopic peak.



Characteristics of the analyzed PS fraction	M_n (g.mol^{-1})	M_w/M_n
SEC	1267	1.02
MALDI-TOF	1131	1.01



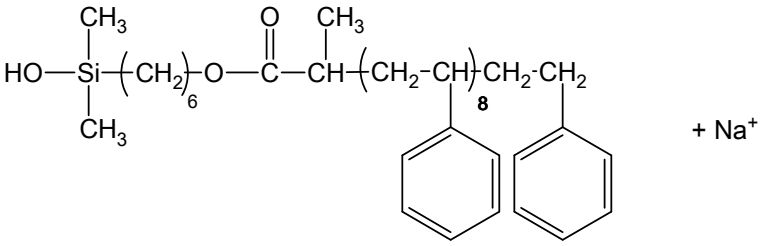
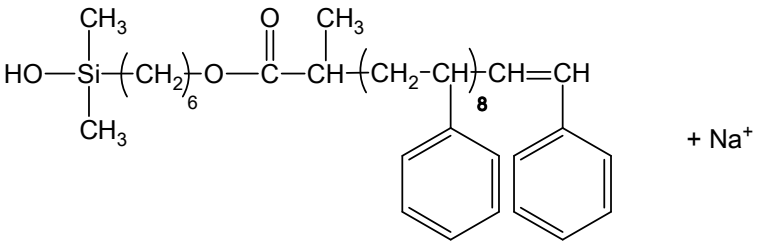
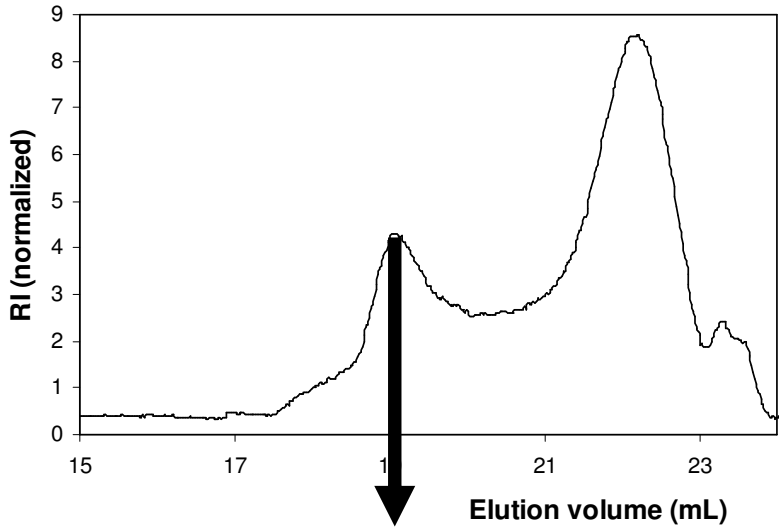
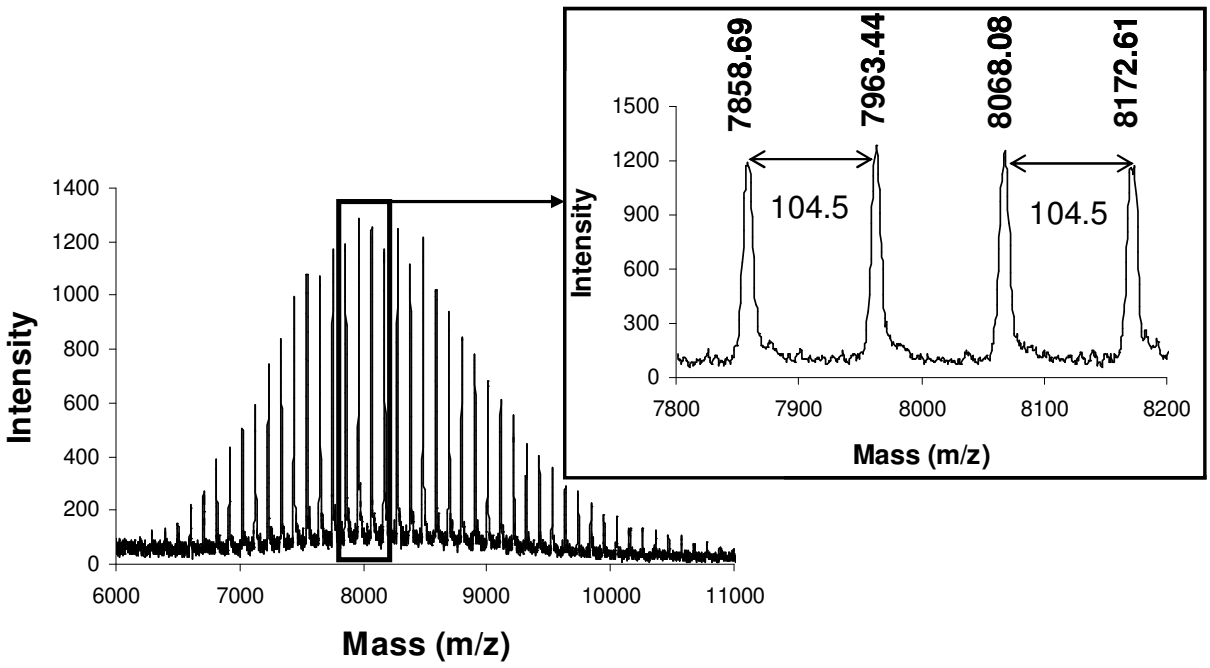
Macromolecular structures	Theoretical molar mass ($g.mol^{-1}$)
	**1191.56532**
	**1189.54967**

Figure SI-10. Analysis of the cleaved PS chains after SI-ATRP of styrene initiated from the micrometric MSU-Brij-BP OMS particles (Expt 17 in table 4): SEC chromatogram and MALDI-TOF spectra (linear mode) of the high M_n fraction recovered after fractionation by semi-preparative SEC.

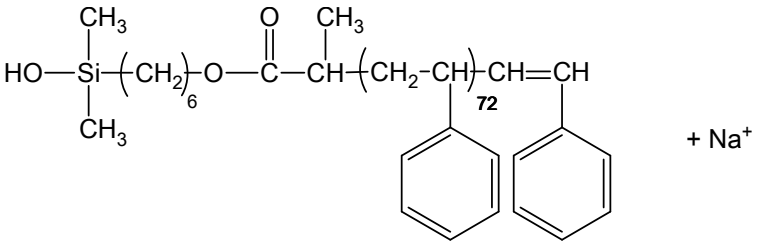


Characteristics of the analyzed PS fraction	M_n (g.mol^{-1})	M_w/M_n
SEC	7570	1.02
MALDI-TOF	8172	1.01



Average atomic mass (g.mol^{-1})					
O	**Br**	**Si**	**C**	**H**	**Na**
15.9994	79.904	28.0855	12.0107	1.0079	22.98977

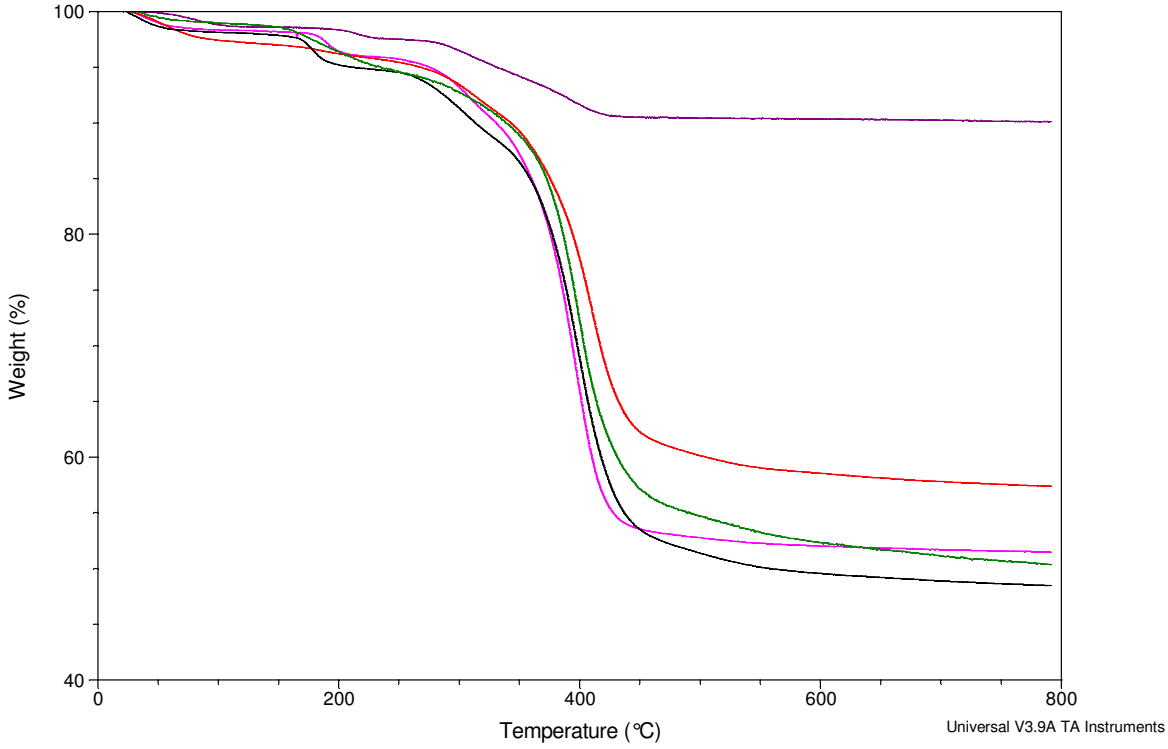
Macromolecular structure



Theoretical molar mass (g.mol^{-1})

7856.22737

Figure SI-11. Overlay of TGA traces for hybrid particles: SN-PMMA (purple), CSSN-30-PMMA (pink), CSSN-45-PMMA (red), CSSN-105-PMMA (black), MCM-41-PMMA (green). See Table 8 in the article for details.



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