Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Ready Access to End-Functional Polystyrenes via a Combination of ARGET ATRP and Thiol−Ene Chemistry

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All manipulations of air-sensitive materials were performed under the rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line interfaced to a high vacuum line (10^{-3} mbar).

Materials

Styrene (99% extra pure, Acros) was destabilized by passing through a basic alumina column and stored at -18 °C. *N*,*N*-dimethylformamide extra dry (DMF) (99.8%, Acros), toluene extra dry (99.8%, Acros), dioxane extra dry (99.8%, Acros), anisole (99.8%, Acros), $CuBr_2$ (99.9%, Acros), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) (97%, Aldrich), tin^{II} 2-ethylhexanoate ($Sn(EH)_2$) (95%, Aldrich), benzyl bromide (BenzBr) (98%, Acros), 1-octanethiol (98.5%, Aldrich), 3-mercaptopropionic (99%, Aldrich), 2-mercaptoethanol (99%, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich) were used as received. Methanol and tetrahydrofuran were purchased as analytical grade (Aldrich) and used as received.

Instrumentation

Size Exclusion Chromatography

Size exclusion chromatography (SEC) measurements were performed on a Polymer Laboratories PL-SEC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50×7.5 mm) followed by three PLgel 5 µm Mixed-C and one PLgel 3 µm Mixed-E columns (300×7.5 mm) and a differential refractive index (DRI) detector using tetrahydrofuran (THF) as the eluent at 35 °C with a flow rate of 1 $mL \cdot min^{-1}$. The SEC system was calibrated using linear polystyrene standards ranging from 467 to $2.5 \cdot 10^6$ $g \cdot mol^{-1}$.

Calculation of the molecular weight proceeded via the Mark-Houwink-Sakurada (MHS) parameters for polystyrene (PS)[1] in THF at 30°C, *i.e.* $K = 14.1\cdot10^{-5}$ dL·g^{-1}, $\alpha = 0.70$.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF-MS)

MALDI-Mass Spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 79.6 µJ (100%) delivered to the sample in 2.2 ns at 100 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode with a resolution (m/Δm) close to 10.000. All the samples were analyzed using trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix Matrix was prepared by dissolution in chloroform (40 mg mL^{-1}). 1µL of the matrix solution was deposited on a stainless-steel target and air dried. Polymer samples were dissolved in chloroform (1 mg mL^{-1}). Aliquots (1µL) of these solutions were deposited onto the target area already bearing the matrix crystals and air dried. Subsequently, 1 µL aliquots of a 0.04 mg mL^{-1} $AgNO_3$ solution in acetonitrile were cast onto the target. For the recording of the single-stage MALDI-MS spectra, the quadrupole (rf-only mode) was set to pass all ions. The ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with an integration time of 1s. Data were acquired in the continuum mode until acceptable averaged data were obtained. Theoretical masses and experimental masses gathered in Table 1 refer to the monoisotopic masses.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The structures of the synthesized compounds were confirmed via ^{1}H-NMR spectroscopy using a Bruker AM 400 MHz. Samples were dissolved in $CDCl_3$. The chemical shift was referenced with tetramethylsilane ($\delta = 0.00$) as internal standard. Abbreviations used below in the description of the materials' syntheses include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

Experimental Section

Synthesis of polystyrene P1 *via* ARGET ATRP

Benzyl bromide (0.21 mL, 1.76 mmol) and tin^{II} 2-ethylhexanoate ($Sn(EH)_2$, 0.357 g, 0.9 mmol) were separately dissolved in anisole (10 mL in total) in round-bottom flasks and purged with argon for 30 min. In a Schlenk flask, equipped with a stirring bar, styrene (20 mL, 0.17 mol), $CuBr_2$ (39.2 mg, 0.176 mmol) and tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 41.4 µL, 0.176) were dissolved in anisole (10 mL) and purged with argon for 30 min. After removing oxygen, the initiator and reducing agent-solution were transferred to the reaction flask *via* a cannula. The reaction mixture was subsequently placed into an oil bath tempered at 90 °C for 2 h. To stop the polymerization process, the flask was cooled to ambient temperature in a water bath and subsequently opened to the atmosphere. The copper catalyst was removed by passing the solution over a short column of neutral alumina oxide. The purified polymer was obtained by two-fold precipitations into methanol. The precipitate was filtered off and dried under high vacuum to afford the polymer as a white powder, yielding 28%, $M_{\mathrm{n,NMR}}$ = 3900 Da, $M_{\mathrm{n,SEC}}$ =

4000 Da, $Đ$ = 1.05. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01-6.39 (5H, aromatic protons of PS), 4.54-4.22 (1H, *CH*-Br), 1.78-1.18 (aliphatic protons of PS).

Synthesis of terminal double bond functional polystyrene P2

The polymer containing a bromine end-group (3 g, polystyrene **P1**, see Scheme 2) was dissolved in 10 mL of DMF in a round-bottom flask. The reaction solution was purged with argon for 20 min and then stirred for 16 h at 100°C in a preheated oil bath. After 16 h, the reaction mixture was cooled and subsequently diluted in ethyl acetate and washed four times with distilled water. The reaction mixture was concentrated under vacuum and the polystyrene precipitated in methanol. The precipitate was filtered off and dried under high vacuum to afford the terminal alkene functional polymer as white powder, $M_{\mathrm{n,NMR}}$ = 4100, $M_{\mathrm{n,SEC}}$ = 4200 Da, $Đ$ = 1.06. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01-6.39 (5H, aromatic protons of PS), 6.08-6.21 (2H, double bond protons), 3.10 (1H, adjacent to double bond protons), 1.78-1.18 (aliphatic protons of PS).

Representative procedure for the synthesis of functional polystyrenes (P3, P4 or P5) using thiol-ene chemistry

Polymer bearing terminal double bond (polystyrene **P2**, see Scheme 2, 0.4 g, 0.1 mmol) was dissolved in 6 mL of dioxane/toluene (v:v =1:1).[2] After complete dissolution, 2,2-dimethoxy-2-phenylacetophenone (DMPA, 25.6 mg, 0.1 mmol) and the thiol compound (i.e. 2-mercaptoethanol, 35 µL, 0.5 mmol) was added. The mixture was irradiated by a 36 W compact fluorescent lamp (λ_{max} = 355 nm) with a 15 cm distance for 16 h at ambient temperature. The purified polystyrene (P4, see scheme 2) was obtained by two times precipitation into methanol. The precipitate was filtered off and dried under high vacuum at ambient temperature to afford the end-functional polymers as white powders. **P3**: $M_{\text{n,NMR}}$ = 4000 Da, $M_{\text{n,SEC}}$ = 4500 Da, $Đ$ = 1.07, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01-6.39 (5H, aromatic protons of PS), 2.51–2.76 (2H, adjacent to thio-ether bond), 1.78-1.18 (aliphatic protons of PS), 0.81 (3H, octanethiol). **P4**: $M_{\text{n,NMR}}$ = 4200 Da, $M_{\text{n,SEC}}$ = 4400 Da, $Đ$ = 1.06, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01-6.39 (5H, aromatic protons of PS), 3.21–3.07 (2H, adjacent to hydroxyl), 2.51–2.76 (2H, adjacent to thio-ether bond), 1.78-1.18 (aliphatic protons of PS). **P5**: $M_{\text{n,SEC}}$ = 4400 Da, $Đ$ = 1.06. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01-6.39 (5H, aromatic protons of PS), 2.51–2.76 (2H, adjacent to thio-ether bond), 1.78-1.18 (aliphatic protons of PS).

Thermal stability assessment of thio-ether functional polystyrenes

For the stability test under inert atmosphere, 10 mL Schlenk tubes were dried with a heat gun and cooled in an argon. The polymer samples (each *ca.* 25 mg) were added to the Schlenk tubes, which were then evacuated for 60 min and refilled with argon. Subsequently, the thermal stability of the samples under inert atmosphere was tested in an oil bath at 120°C, 140°C, 160°C, 180°C and 200°C for 24 h.

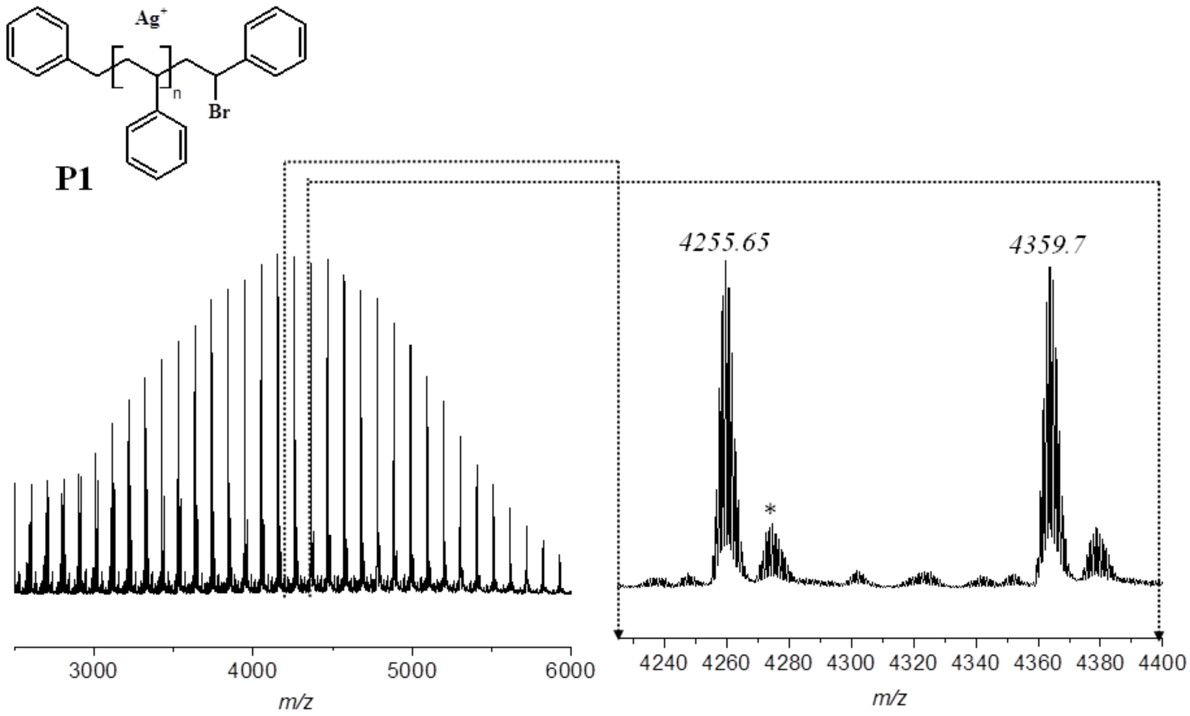

Figure S1. MALDI-ToF-MS spectrum of polystyrenes **P1**, $AgNO_3$ used as cationization agent. *Refers to hydroxyl-functionalized PS.[3]

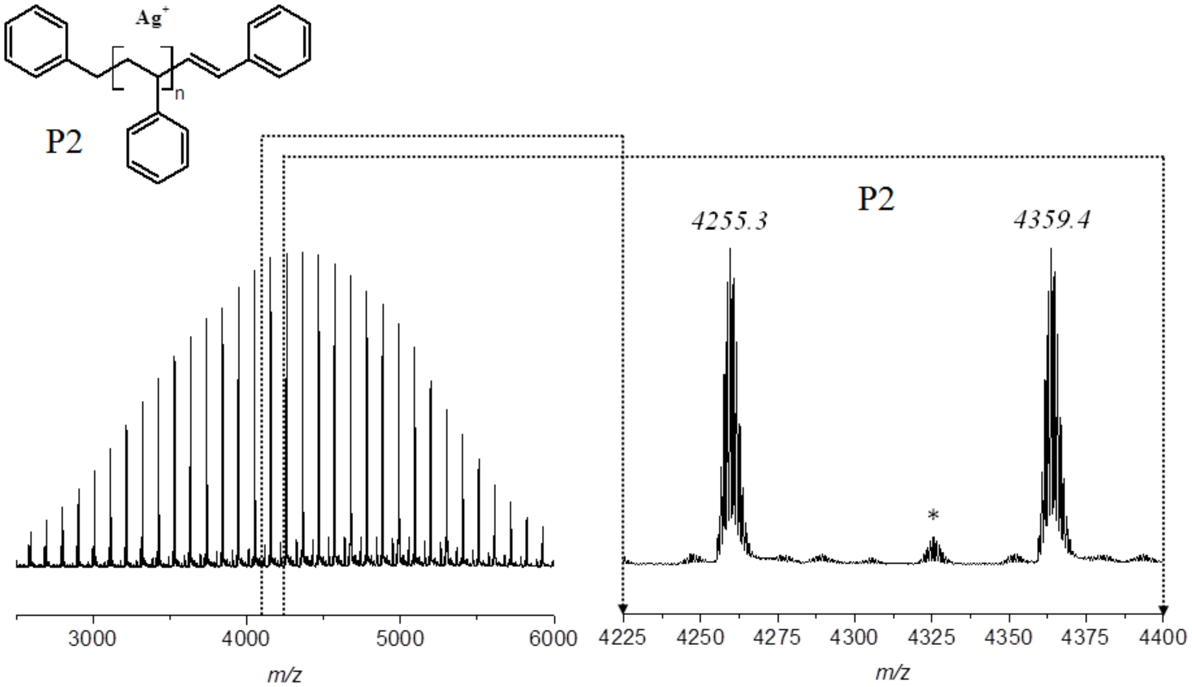

Figure S2. MALDI-ToF-MS spectrum of polystyrenes **P2**, $AgNO_3$ used as cationization agent.

*Refer to PS chains cationized by $Ag_2NO_3^+$.

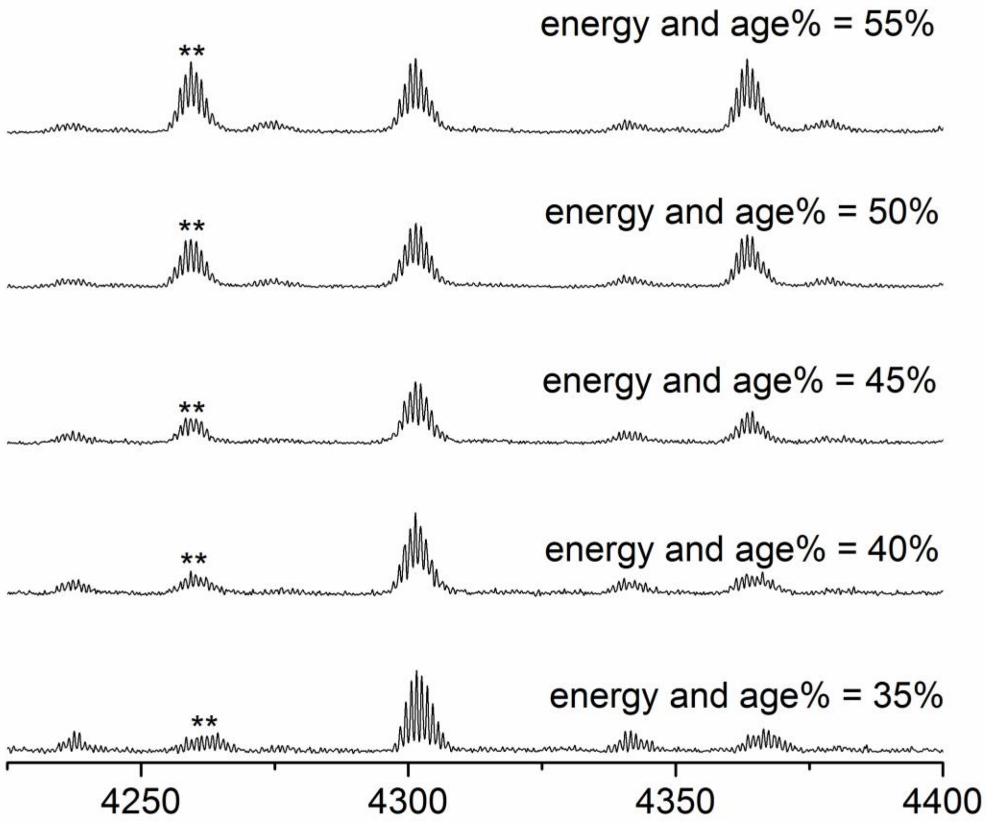

Figure S3. MALDI-ToF-MS spectra of **P3** at increasing laser energy from 35% to 55% of the maximum output corresponding to 79.6 µJ per pulse. J cm^{-2}. ** Refers to fragmented ions during the MALDI ionization processes.

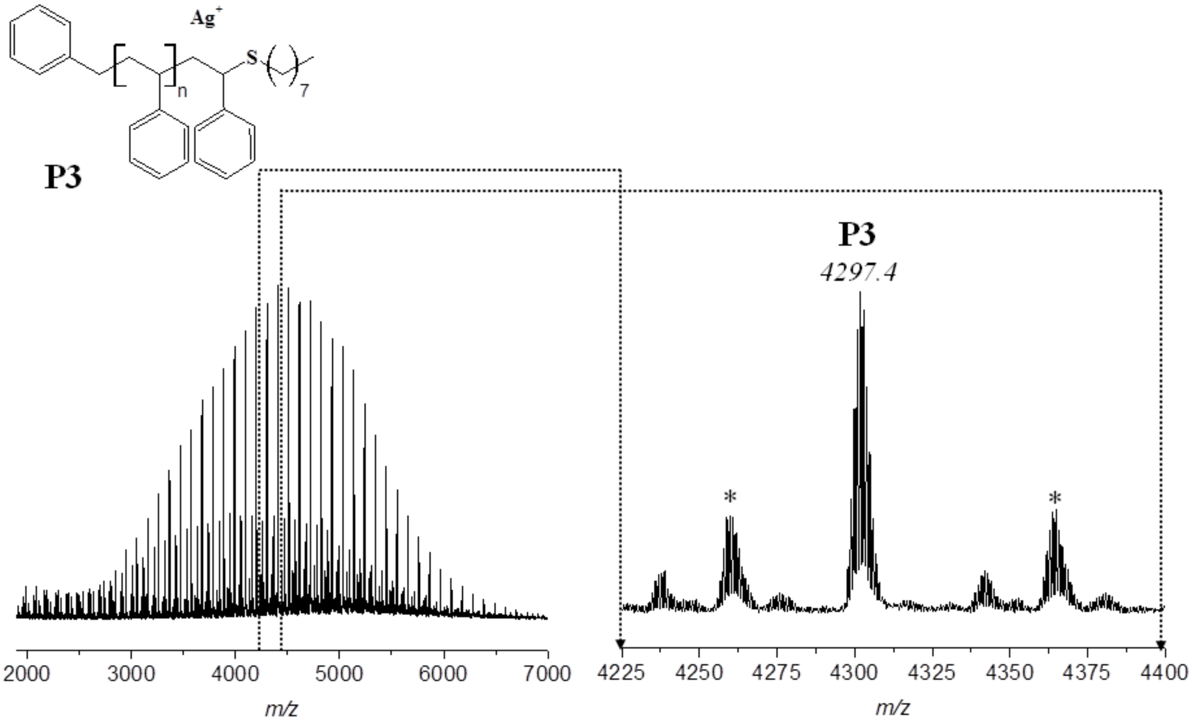

Figure S4. MALDI-ToF-MS spectrum of polystyrenes **P3**, $AgNO_3$ used as cationization agent. *Created upon the MALDI ionization processes.

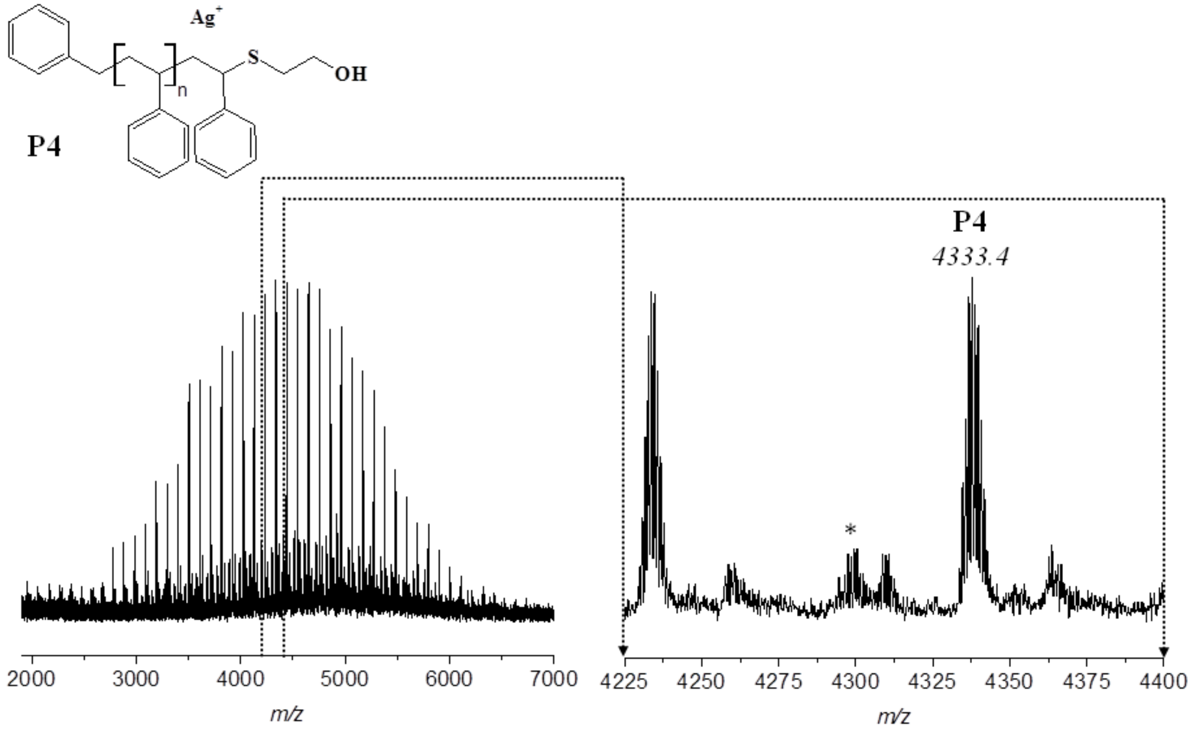

Figure S5. MALDI-ToF-MS spectrum of polystyrenes **P4**, $AgNO_3$ used as cationization agent. *Refer to PS chains cationized by $Ag_2NO_3^+$.

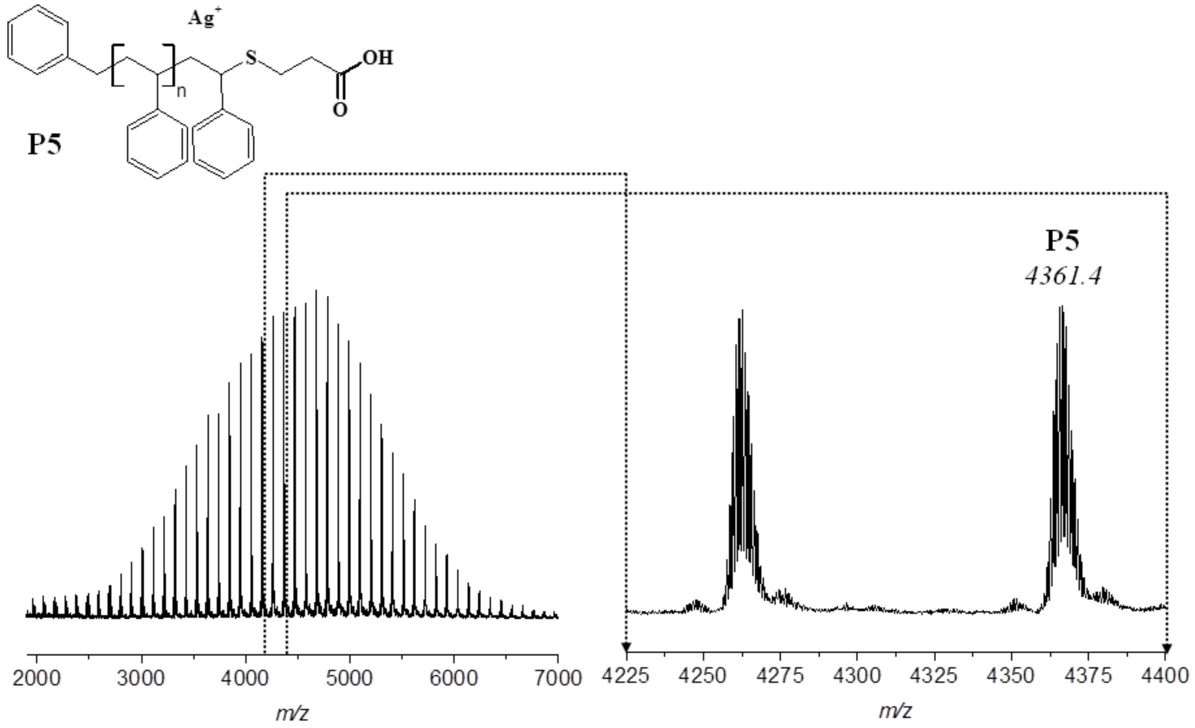

Figure S6. MALDI-ToF-MS spectrum of polystyrenes **P5**, $AgNO_3$ used as cationization agent. *Refer to PS chains cationized by $Ag_2NO_3^+$.

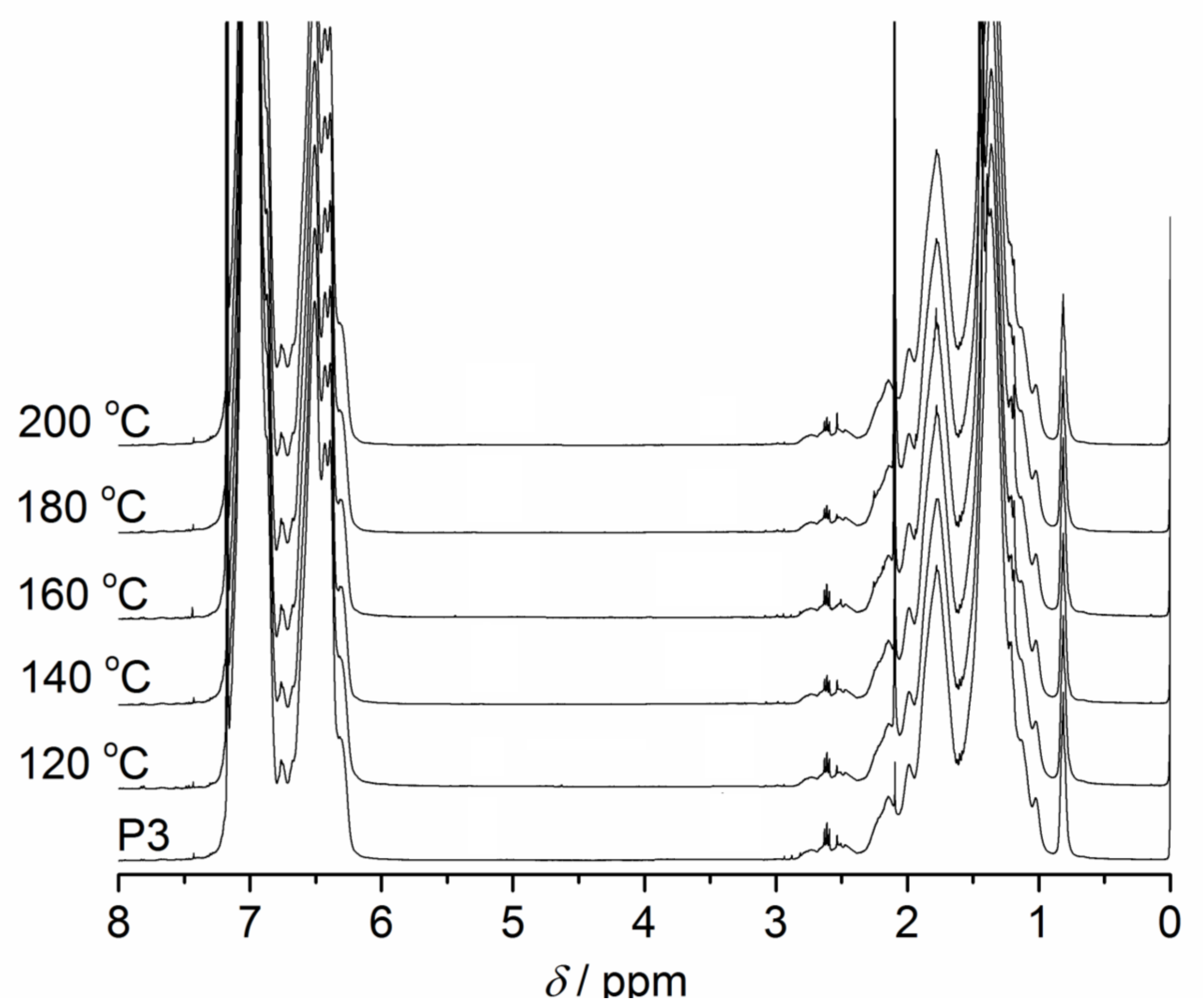

Figure S7. ^{1}H NMR spectra of polystyrene **P3** as well as after thermal treatment of P3 at various temperature for 24 h under an argon atmosphere recorded in $CDCl_3$ at ambient temperature.

REFERENCES

1. C. Strazielle, H. Benoit and O. Vogl, *Eur. Polym. J.*, 1978, **14**, 331-334.
2. B. B. Uysal, U. S. Gunay, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 1581-1587.
3. O. Altintas, T. Josse, M. Abbasi, J. De Winter, V. Trouillet, P. Gerbaux, M. Wilhelm and C. Barner-Kowollik, *Polym. Chem.*, 2015, **6**, 2854-2868.