Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

ATRP-based Polymers with Modular Ligation Points under Thermal and Thermomechanical Stress

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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. 6-Bromohexanol (97%, ABCR GmbH and Co. KG), ethylenediaminetetraacetic acid disodium salt (EDTA) (99%, Acros), 4-dimethylamino pyridine (DMAP) (99%, Acros), *N*,*N*-dimethylformamide extra dry (DMF) (99.8%, Acros), anisole (99.8%, Acros), tetrahydrofuran (THF) extra dry (99.8%, Acros), sodium azide (99.8%, Acros), α-bromo isobutyric acid (98%, Aldrich), propargyl alcohol (99%, Aldrich), $CuBr_2$ (99.9%, Acros), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) (97%, Aldrich), tin^{II} 2-ethylhexanoate ($Sn(EH)_2$) (95%, Aldrich), cupric sulfate pentahydrate (99.5%, Aldrich), (+)-sodium L-ascorbate (98%, Aldrich), decyl bromide (99.8%, Aldrich), tributyltin hydride (97%, Aldrich), 3-(trimethylsilyl)propargyl bromide (**TMSPrBr**) (97%, Aldrich), tetrabutylammonium fluoride (1M solution in THF, Alfa-Aesar), benzyl bromide (**BenzBr**) (98%, Acros), methyl 2-bromoisobutyrate (**MBr*i*B**) (98%, Aldrich) and ethylene bis(2-bromoisobutyrate) (**E*b*Br*i*B**) (99%, Aldrich) were used as received. Methanol, cyclohexane, ethyl acetate 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 $\text{mL}\cdot\text{min}^{-1}$. The SEC system was calibrated using linear polystyrene standards ranging from 467 to $2.5\cdot10^{6}$ $\text{g}\cdot\text{mol}^{-1}$. Calculation of the molecular weight proceeded via the Mark-Houwink-Sakurada (MHS) parameters for polystyrene (PS)[1] in THF at 30°C, *i.e.* $K = 14.1\cdot10^{-5}$ $\text{dL}\cdot\text{g}^{-1}$, $\alpha = 0.70$.

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 nitrogen laser, operating at λ=337 nm with a maximum output of 500 J m^{-2} delivered to the sample in pulses of 4 ns at a repeating rate of 20 Hz. Time-of-flight mass analyses were performed in the reflectron mode with a resolution ($m/\Delta m$) close to 10.000. The matrix *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was prepared by dissolution in chloroform (40 mg mL^{-1}). 1 µL 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 (1 µL) of these solutions were deposited onto the target area already bearing the matrix crystals and air dried. Subsequently, 1 µL aliquots of a 1 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 1 s. Data were acquired in the continuum mode until acceptable averaged data were obtained. Theoretical masses are monoisotopic for the most common isotope.

X-Ray Photoelectron Spectroscopy (XPS)

XPS Investigations were performed on a K-Alpha spectrometer (ThermoFisher Scientific, East Grinstead, UK) using a microfocused and monochromated Al Kα X-ray source (400 µm spot size). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. Data acquisition and processing using the Thermo Avantage software is described elsewhere.[2] The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: ±0.2 eV). The analyzer transmission function, Scofield[3]sensitivity factors and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[4] All spectra were referenced to the C1s peak (C-C, C-H) at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag and Au.

Sample preparation and rheometry

Polystyrene powder was shaped under the hot press into disks with 25 mm diameter and 1 mm thickness at 180 °C under vacuum condition to remove any trapped air or residual volatile solvents. The total resident time of the sample under hot press at temperature higher than 120 °C was less than 5 minutes to ensure that there was no chemical change (e.g. cleavage or degradation) during the sample preparation. The sample was removed from the press at ambient temperature. All samples were checked visually to ensure that they showed no cracks or trapped air. The rheological characterization of the polymer melts was carried out under a nitrogen atmosphere using a forced convection oven in an advanced rheometric expansion system (ARES-G2) rheometer from TA Instruments. Small amplitude oscillatory shear (SAOS) measurements were conducted using a parallel plate geometry (25 mm diameter, gap ≈ 1 mm) at 180 °C. Dynamic time sweep test were carried out at $\gamma_0 = 15\%$ and a frequency 0.05 Hz. The complex viscosity, $\eta^*_{(\omega,t)}$, was measured to follow the polymer degradation as a function of time. Dynamic frequency sweep tests ($G'_{(t)}$, $G''_{(t)}$) were performed in the frequency range from $\omega_1/2\pi = 0.01$ Hz to 15 Hz to ensure that the measured complex viscosity at the frequency of 0.05 Hz is equal to the zero shear viscosity η_0 according to the Cox-Merz rule.[5,6]

Extrusion

A Haake Minilab (Thermo Fisher Scientific) twin screw extruder was used to extrude and circulate the polymer melt under typical processing conditions. This extruder is especially developed for the compounding of small volume samples of up to 5 g. The twin screw extruder was operated in counter rotating mode, the required extrusion time (20 min as a typical mean residence distribution time for industrial extrusion) for the mixture could be readily controlled at 200 °C. At the end of the extrusion experiment, the re-circulation was stopped by opening the bypass valve and extruding the sample as a rod allowing for subsequent molecular characterization.

Synthesis

Synthesis of the bifunctional ATRP initiator carrying a triazole unit (6)

4 (see Scheme 2) (1 g, 3.4 mmol), **5** (0.77 g, 3.76 mmol), copper (II) sulfate pentahydrate (0.17 g, 0.68 mmol) and sodium ascorbate (0.136 g, 0.68 mmol) were dissolved in *N*,*N*-dimethylformamide (DMF) (10 mL). The resulting mixture was stirred at ambient temperature overnight. The reaction mixture was diluted in 200 mL of ethyl acetate and extracted two times with 50 mL of ethylenediaminetetraacetic acid disodium salt (EDTA) aqueous solution (5%) to remove Cu. The organic phase was dried over Na_2SO_4 and the solution was subsequently concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel with ethyl acetate / hexane (1:1) to give the product **6** as pale yellow liquid (1.53 g, isolated yield: 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 5.26 (s, 2H), 4.30 (t, *J* = 7.2 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.86 (s, 12H), 1.67 – 1.52 (m, 4H), 1.45 – 1.17 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.68, 171.53, 142.26, 123.56, 65.67, 59.26, 55.97, 55.69, 50.27, 30.76, 30.65, 30.11, 28.15, 26.04, 25.27. ESI-MS $(M+Na)^+$ $C_{17}H_{27}Br_2N_3O_4Na$ theoretical: 518.03 Da, experimental: 518.25 Da.

General procedure of ARGET ATRP of styrene

The initiator and tin^{II} 2-ethylhexanoate ($Sn(EH)_2$) were separately dissolved in anisole in round bottom flasks and purged with argon for 30 min. In a Schlenk flask, equipped with a stirring bar, styrene, $CuBr_2$ and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) were dissolved in anisole 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 the appropriate reaction time (refer to

Table 1). To stop the polymerization process, the flask was opened to the atmosphere and cooled to ambient temperature in a water bath. The copper catalyst was removed by passing the solution over a short column of neutral alumina oxide when more than 5 ppm of Cu was used. The purified polymer was obtained by two fold precipitations into methanol. The precipitate was filtered off and dried under high vacuum to afford the polymers as white powders.

General procedure for the deprotection of the acetylene moiety

Polymer bearing TMS protected acetylene end groups (polystyrene **9**, see Scheme 2) was dissolved in tetrahydrofuran (THF) (0.01 M solution). After complete dissolution, a solution of tetrabutylammonium fluoride (TBAF) (10 eq.) in THF (1.0 M) was added and the reaction mixtures were stirred for 16 h at ambient temperature. The polystyrene was purified using a basic alumina column to remove the residual salts. The purified polystyrene was obtained by two-fold precipitation into methanol. The precipitate was filtered off and dried under high vacuum at ambient temperature to afford alkyne functional polymers as white powder .

General procedure for the synthesis of azide end-functionalized polymers

Polymer containing bromine end groups (polystyrene **1**, see Scheme 2) was dissolved in DMF. Subsequently, NaN_3 (30 eq.) was added and the reaction mixture was stirred for 20 h at ambient temperature.[7] Next, the reaction mixture was diluted in ethyl acetate and washed four times with distilled water. The reaction mixture was concentrated in vacuum and the polystyrene precipitated in methanol. The precipitate was filtered off and dried under high vacuum to afford the azide functional polymer as white powder.

Synthesis of block homopolymer (PS-*b*-PS) *via* CuAAC ligation

8 (1 g, 0.5 mmol), **10** (1.05 g, 0.5 mmol), copper (II) sulfate pentahydrate (0.25 g, 1 mmol) and sodium ascorbate (0.2 g, 1 mmol) were dissolved in DMF (10 mL). The resulting mixture was stirred at ambient temperature overnight. The reaction mixture was diluted in 200 mL of ethyl acetate and extracted two times with 50 mL of 5% EDTA solution to remove Cu. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The purified polystyrene was obtained by two fold precipitations into methanol. The precipitate was filtered off and dried under high vacuum to afford the block homopolymer as a white powder.[8]

General procedure for the dehalogenation of polystyrenes prepared by ARGET ATRP

The polystyrenes prepared by ARGET ATRP (1 eq., i.e. 1 g of polymer **7a**) and tributyltin hydride (50 eq.) were dissolved in toluene (20 mL) and purged with argon for 60 min. Subsequently, the mixture was stirred at 85 °C for 3 h and filtered through a short column of basic alumina (eluent THF). After removal of the THF in vacuum, the residue was again dissolved in a small amount of THF and the solution was poured into methanol under vigorous stirring. The purification by precipitation was conducted three times. The precipitated polymer was collected and dried in vacuum.[9] The characterization data as well as the full molecular weight distributions for the polymers can be found in Figure 1 and Table 1b.

General procedure for the treatment of polystyrenes with decyl bromide

Polystyrene **7b** (1 eq., 0.3 g) and decyl bromide (20 eq.) were dissolved in DMF (0.5 mL) in a 10 mL Schlenk tube and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under argon. The reaction was performed at 100 °C for 24 h and subsequently were stopped by cooling the reaction flask with liquid nitrogen. The solvent was removed in vacuum and the crude mixture was dissolved in THF and precipitated in methanol three times. The precipitate was filtered off and dried under high vacuum to afford the polymer as white powder.

Thermal Treatment

10 mL Schlenk tubes for degradation under inert atmosphere were first dried with a heat gun without polymer and cooled under argon. The polymer samples (each ca. 5 mg) were added into the Schlenk tube and deoxygenated for 60 min and left under argon. Subsequently, the thermal degradation of the samples under inert atmosphere (nitrogen or argon) was carried out in an oil bath at the noted temperatures for pre-set time intervals.

Synthesis and Characterization of the Polymer Library

To allow for an in-depth characterization of the degradation process on the molecular level, polymers of small molecular weight were prepared (refer to Table 1) in addition to large polymer systems, in order to understand the degradation on a molecular level via mass spectrometry and NMR techniques. In the current study, the core-first and the arm-first strategies were applied to obtain triazole mid-chain functional linear polystyrenes. Initially, a bifunctional ATRP initiator carrying a triazole unit was synthesized via CuAAC based on **4** and **5** in the presence of a $CuSO_4 \times 5H_2O$ and sodium ascorbate catalyst system and DMF as solvent. The crude product was purified via column chromatography. The structure and its purity was determined by ESI-MS, ^{1}H NMR and ^{13}C NMR (refer to Figure S1 and S2). The ^{1}H NMR spectrum of **6** indicates that the characteristic proton resonances for the CH_2 next to the triazole unit and $COC(CH_3)_2Br$ are observed at 4.36 ppm and 1.92 ppm, respectively.

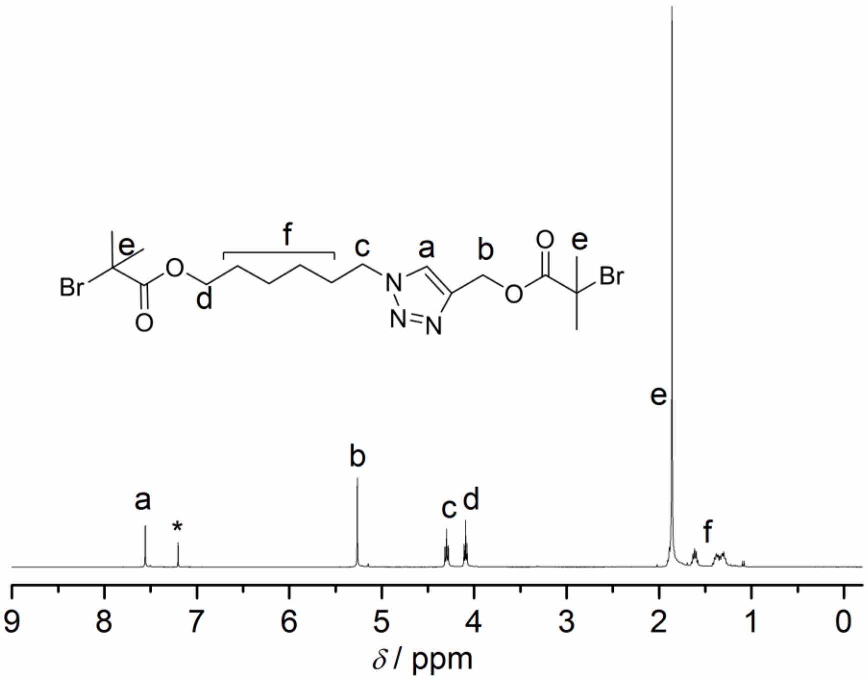


Figure S1. ^{1}H NMR spectrum of (1-(6-((2-bromo-2-methylpropanoyl)oxy)hexyl)-1*H*-1,2,3-triazol-4-yl)methyl 2-bromo-2-methylpropanoate (**6**) in $CDCl_3$ at ambient temperature. The resonance marked with an asterisk is due to solvent ($CHCl_3$).

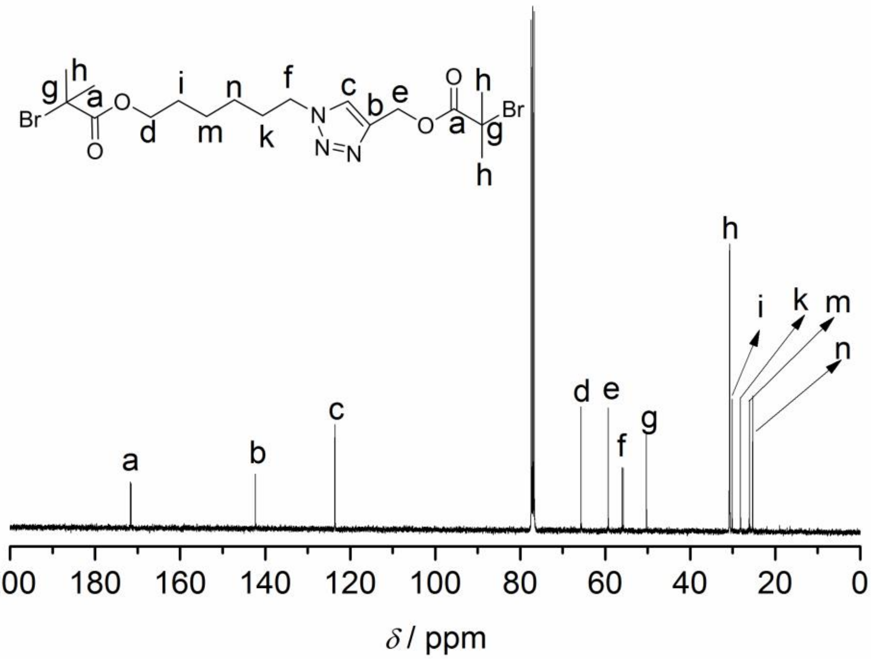


Figure S2. ^{13}C NMR spectrum of (1-(6-((2-bromo-2-methylpropanoyl)oxy)hexyl)-1*H*-1,2,3-triazol-4-yl)methyl 2-bromo-2-methylpropanoate (**6**) in $CDCl_3$ at ambient temperature.

The arm-first technique was additionally employed to prepare a macromolecular structure featuring a triazole unit in the middle of the polymer chain without any additional functional groups. A diblock homopolymer (**11**) was modularly synthesized based on a well-defined azide-end-functionalized polystyrene (**8**) and an alkyne-end functionalized polystyrene (**10**) via a copper-catalyzed azide alkyne cycloaddition. The first step towards the diblock homopolymer (**11**) was to prepare polymeric building blocks with azide (**8**) as well as protected acetylene end groups (**10**). The most appropriate method to introduce a terminal acetylene functionality is to use functionalized initiators, see Scheme 2 in the main text. Thus, TMS-protected acetylene-bearing polystyrene (**9**) was prepared by ARGET ATRP of styrene using TMS-propargyl bromide as initiator under ARGET conditions. The acetylene terminus of polystyrene (**9**) was quantitatively deprotected to afford alkyne functional polystyrene (**10**) according to an ^{1}H NMR assessments using a TBAF based protocol. The resonances of the methyl groups of TMS at 0.03 ppm vanished and a new resonance associated with the alkyne terminal proton appeared at 2.43 ppm (refer to Figure S3). However, the resonances indicate that the bromine at the opposite chain terminus (resonances at 4.30 to 4.65 ppm) also disappeared after TBAF treatment and a new set of resonances appeared between 6.08 to 6.21 ppm and 3.10 ppm (see Figure S3). These observations suggest that HBr elimination occurred in the presence of TBAF.[10] The bromine end group of polystyrene (**1**) were converted by sodium azide to obtain the azide functional polystyrene (**8**) via nucleophilic substitution. The presence of azide functionality on polystyrene (**8**) is underpinned by the appearance of the respective absorptions in the FT-IR spectra (2090 cm^{-1}) and a complete upfield shift of the resonances associated with methine protons adjacent to the end groups in the ^{1}H NMR spectrum (see Figure S3 and S4).

The alkyne functionalized polystyrene (**10**) and azide functionalized polystyrene (**8**) were ligated using $CuSO_4 \times 5H_2O$/Na ascorbate as a catalyst system. Comparing the ^{1}H NMR spectra of **8** and **10** with that of the PS-*b*-PS diblock homopolymer (see Figure S3) indicates that the characteristic proton resonances associated with peak of $\mathit{CH_2}$-N_3 at 3.90 ppm and $\mathit{HC}CCH_2$ disappeared and new proton resonances related to CH_2 next to the triazole ring at 5.00 ppm emerged, evidencing the successful ligation between the azide group and alkyne group. The ligation was further supported by the FT-IR spectrum (see Figure S4). Compared with the FT-IR spectrum of **10**, the characteristic signal of the azide at 2090 cm^{-1} disappeared.

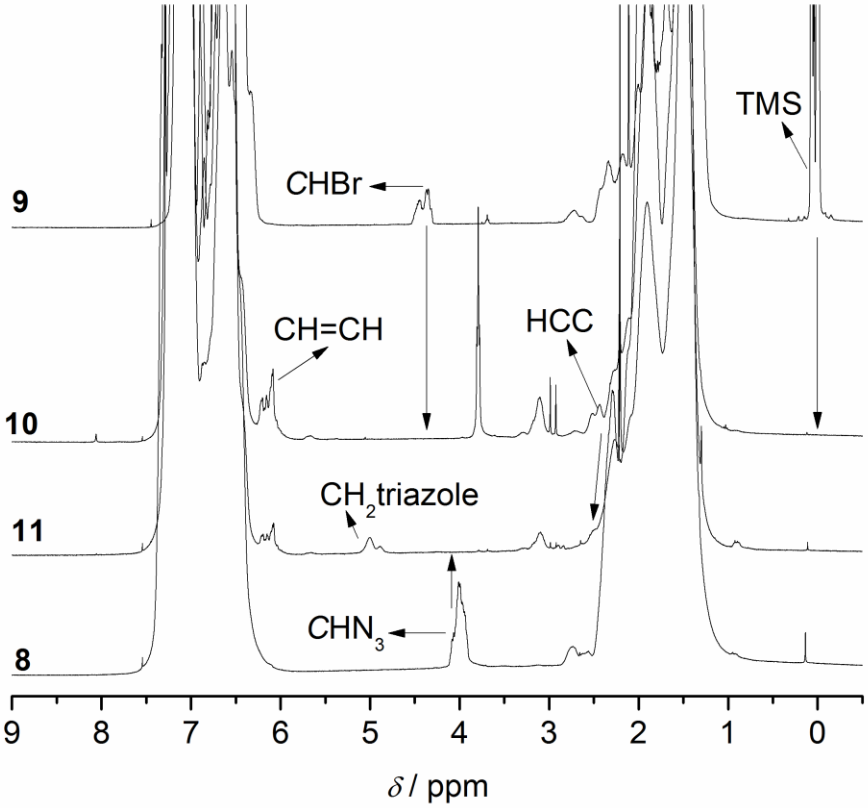


Figure S3. ^{1}H NMR spectra of polystyrene (**9**), after TBAF treatment (**10**), azide functional polystyrene (**8**), after modular ligation (**11**) between (**8**) and (**10**) in CDCl$_3$ at ambient temperature.

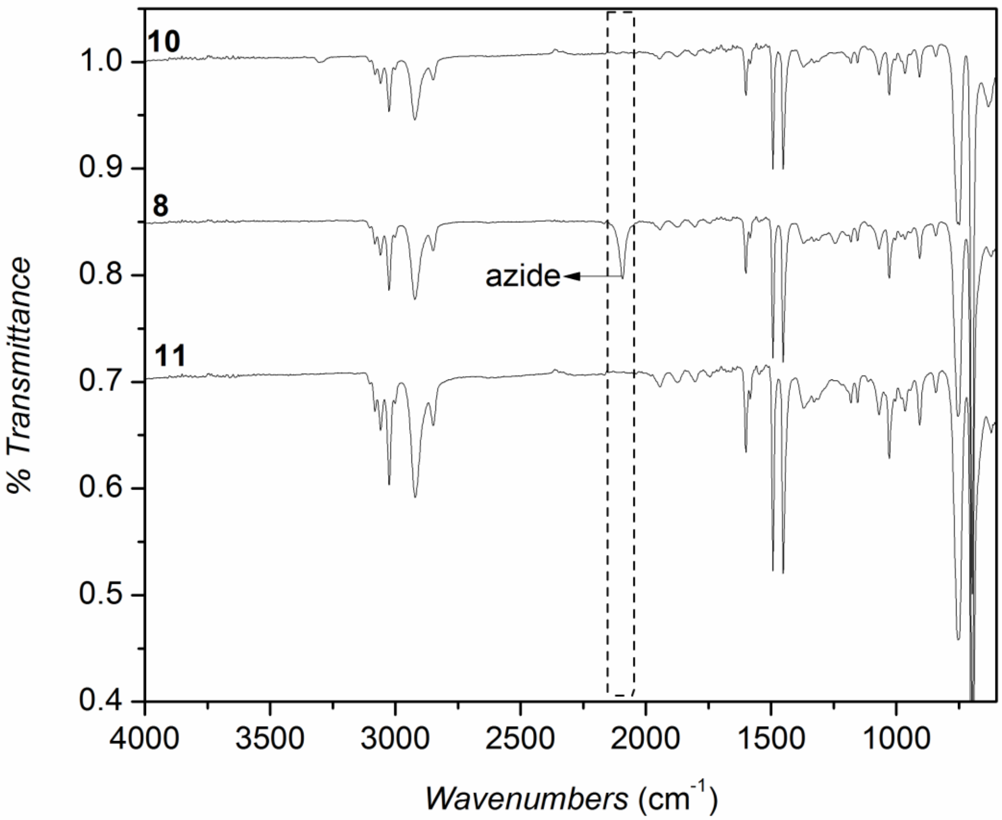


Figure S4. Evolution of the ATR-IR spectra of azide functional polystyrene (**8**), alkyne functional polystyrene (**10**) and ligated polystyrene-*block*-polystyrene (PS-*b*-PS) (**11**).

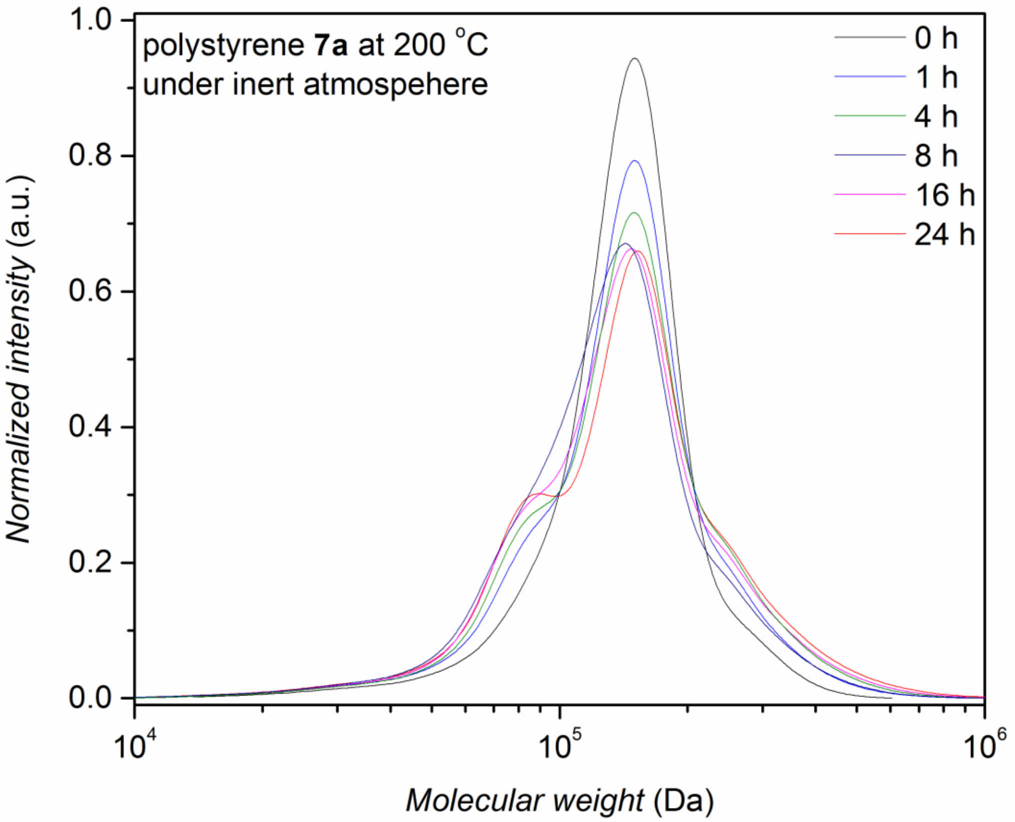


Figure S5. SEC traces of polystyrene **7a** after thermal treatment at 200 °C in an argon atmosphere as a function of time; 0 h (M_n = 119.2 kDa, $Đ$ = 1.19), 1 h (M_n = 112 kDa, $Đ$ = 1.34), 4 h (M_n = 107.7 kDa, $Đ$ = 1.41), 8 h (M_n = 112.9 kDa, $Đ$ = 1.36), 16 h (M_n = 103.5 kDa, $Đ$ = 1.37), 24 h (M_n = 107.9 kDa, $Đ$ = 1.46). All peaks were normalized to total peak area.

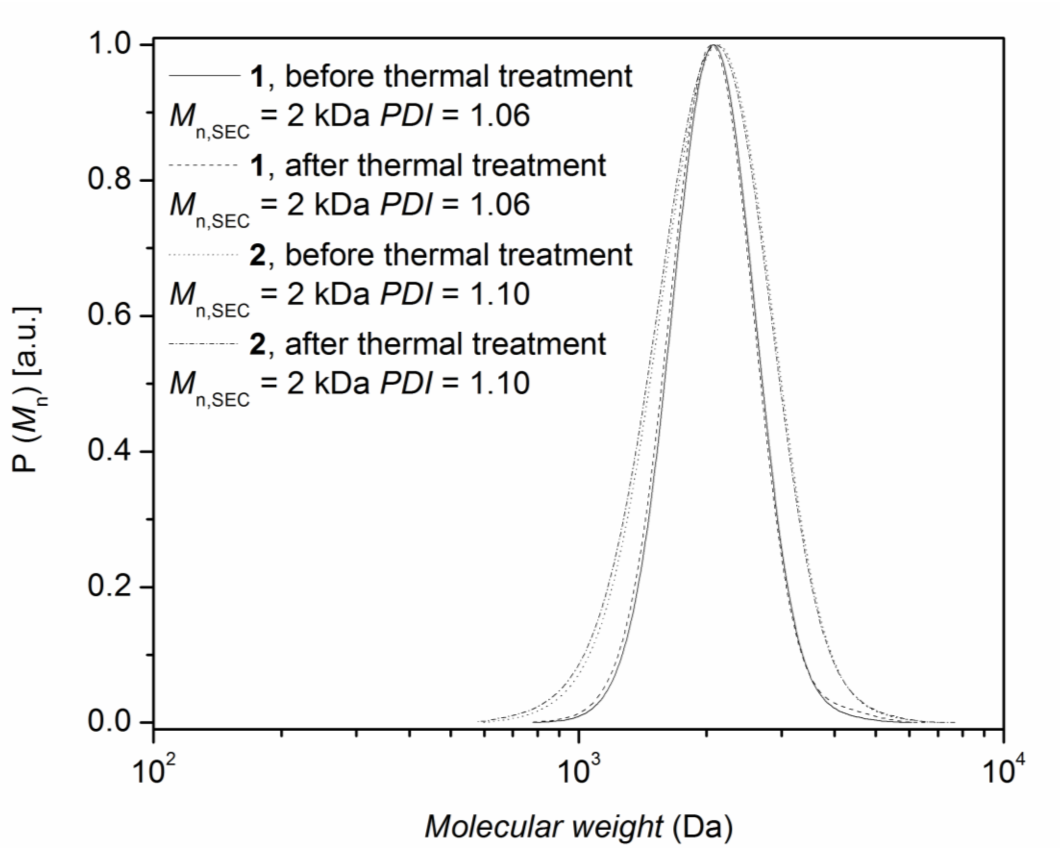


Figure S6. SEC traces the polystyrenes **1** and **2** before and after thermal treatment at 200 °C for 24 h in a nitrogen atmosphere, M_n is given in Da.

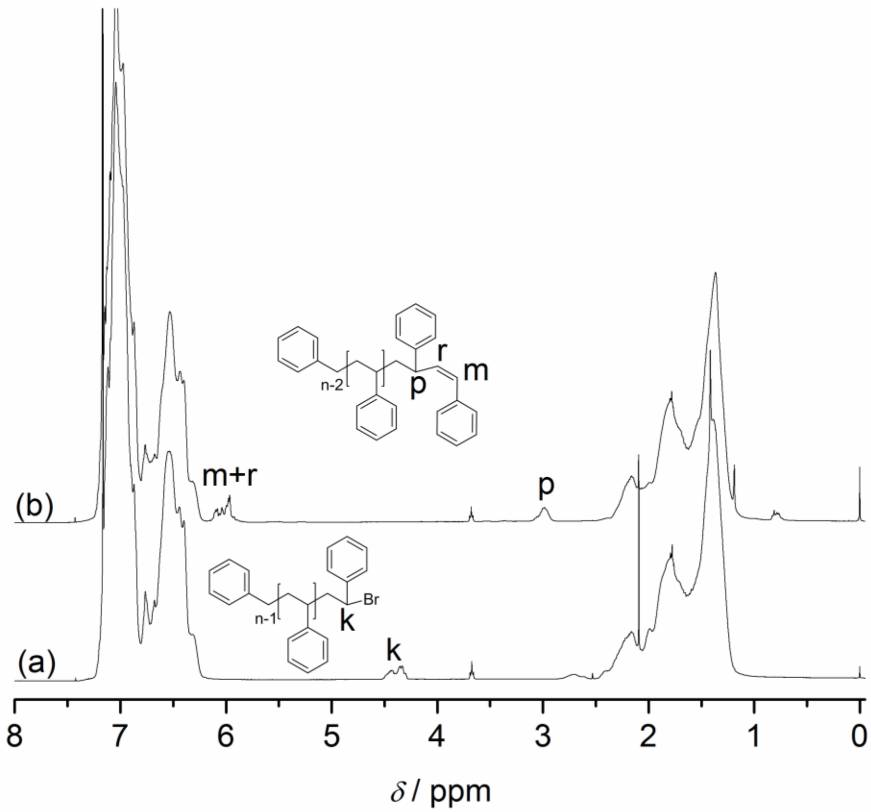


Figure S7. ^{1}H NMR spectra of polystyrene **1** recorded in $CDCl_3$ at ambient temperature: (a) before thermal treatment (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.

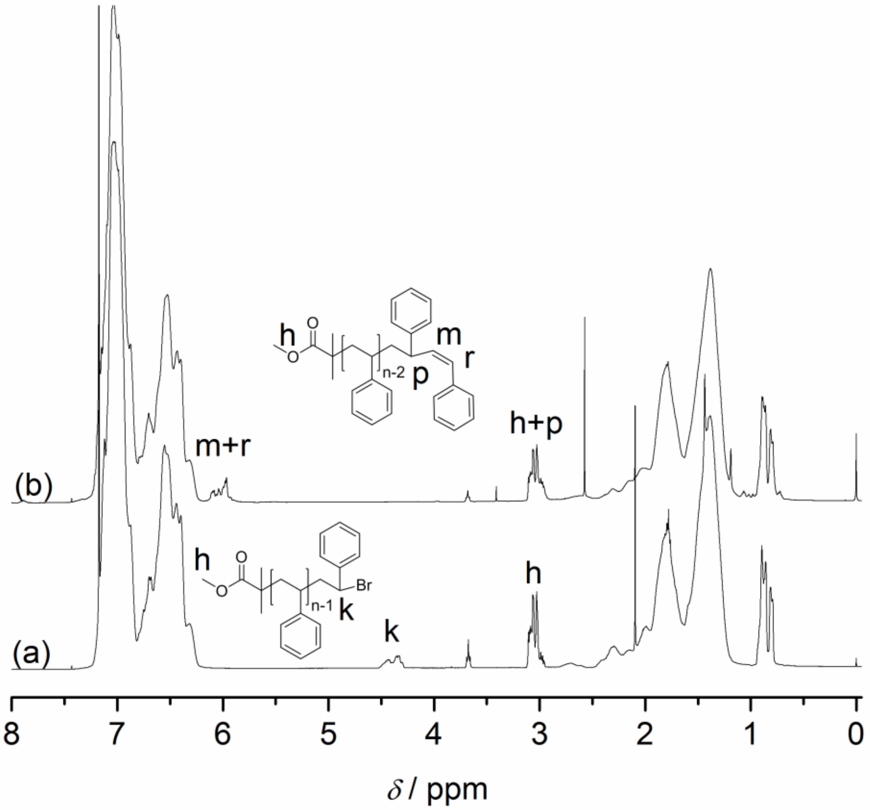


Figure S8. ^{1}H NMR spectra of polystyrene **2** recorded in $CDCl_3$ at ambient temperature: (a) before thermal treatment (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.

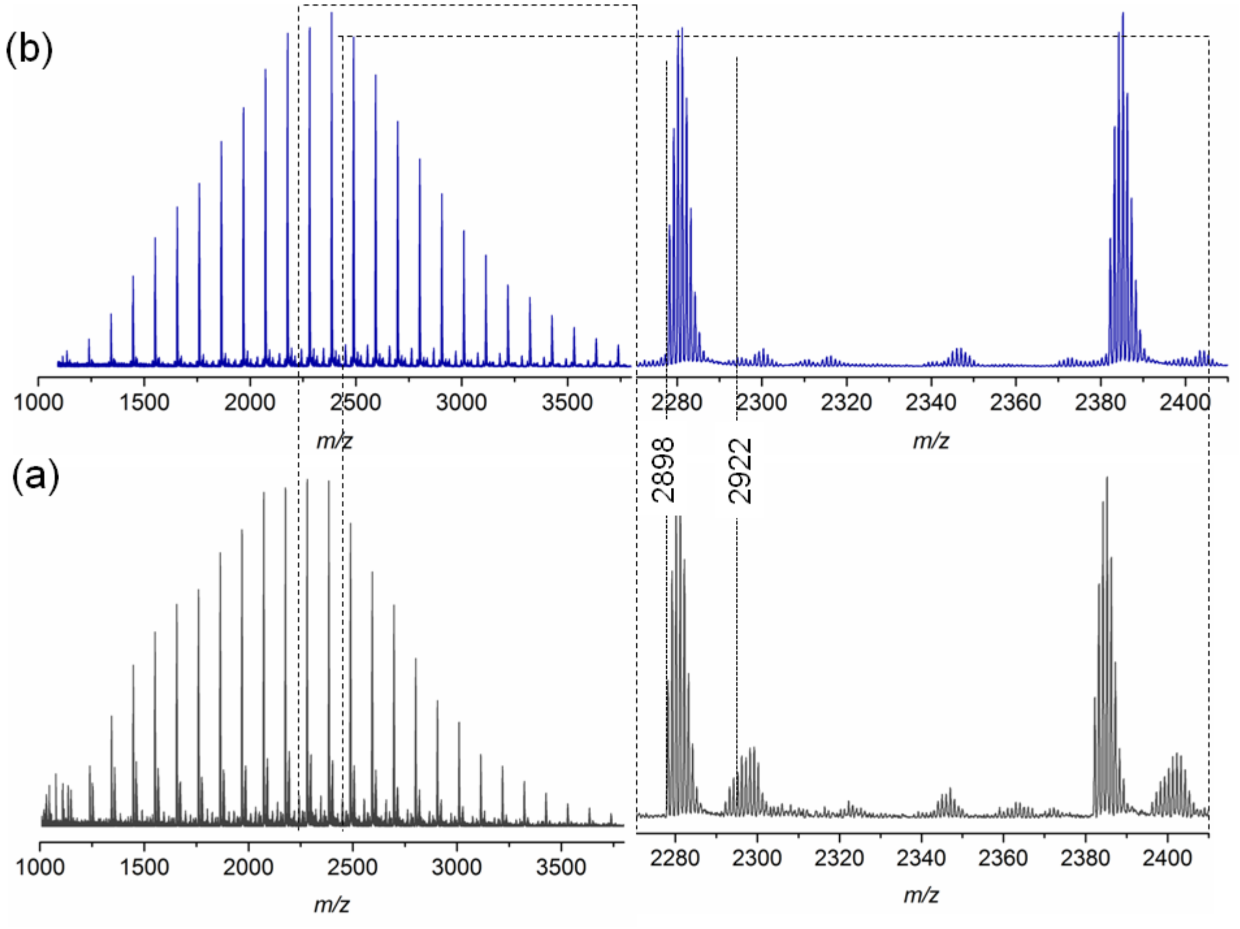
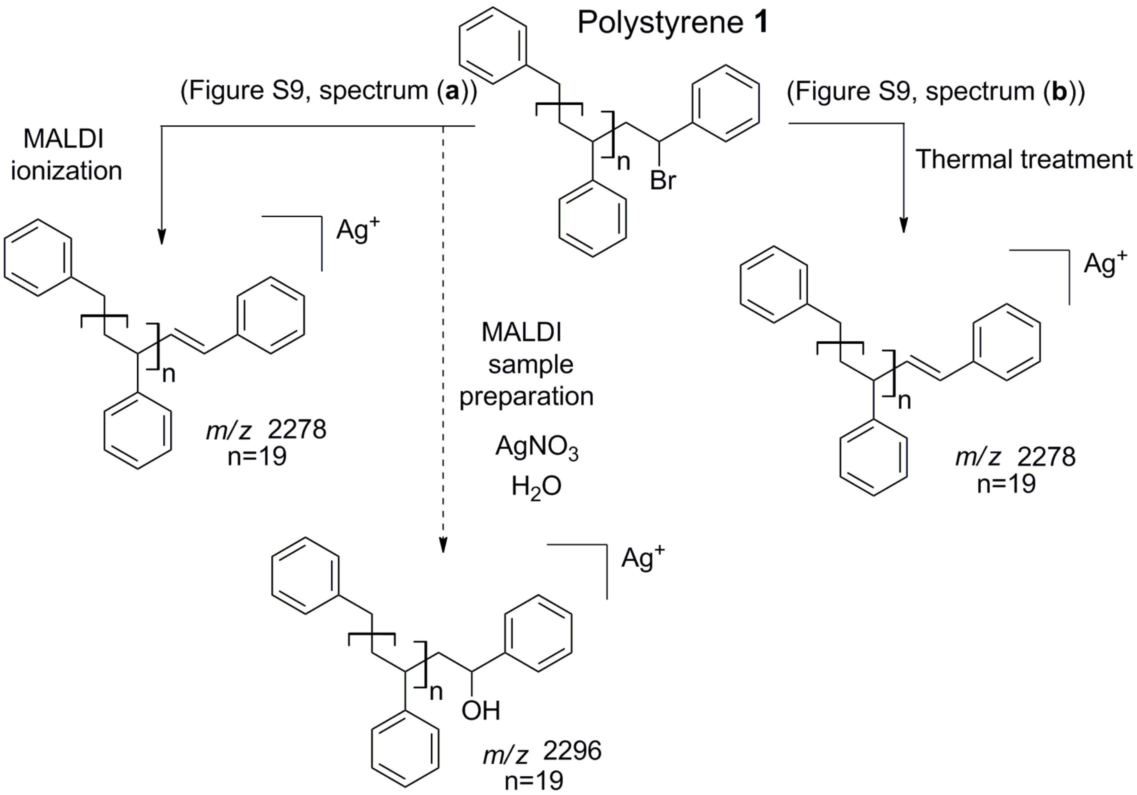


Figure S9. MALDI-MS spectra of polystyrene **1**: (a) before and (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.



Scheme S1. Description of the processes involved following the MALDI ionization of polymer **1** (a) before and (b) after thermal treatment.

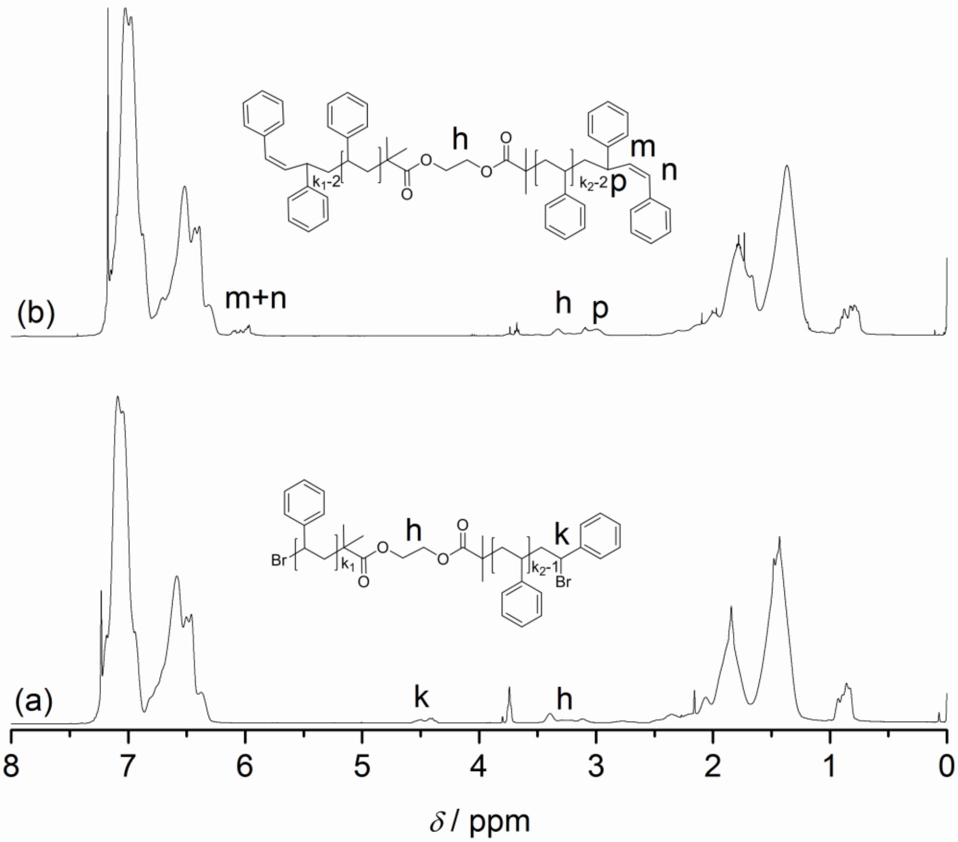


Figure S10. ^{1}H NMR spectra of polystyrene **3a** recorded in $CDCl_3$ at ambient temperature: (a) before thermal treatment and (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.

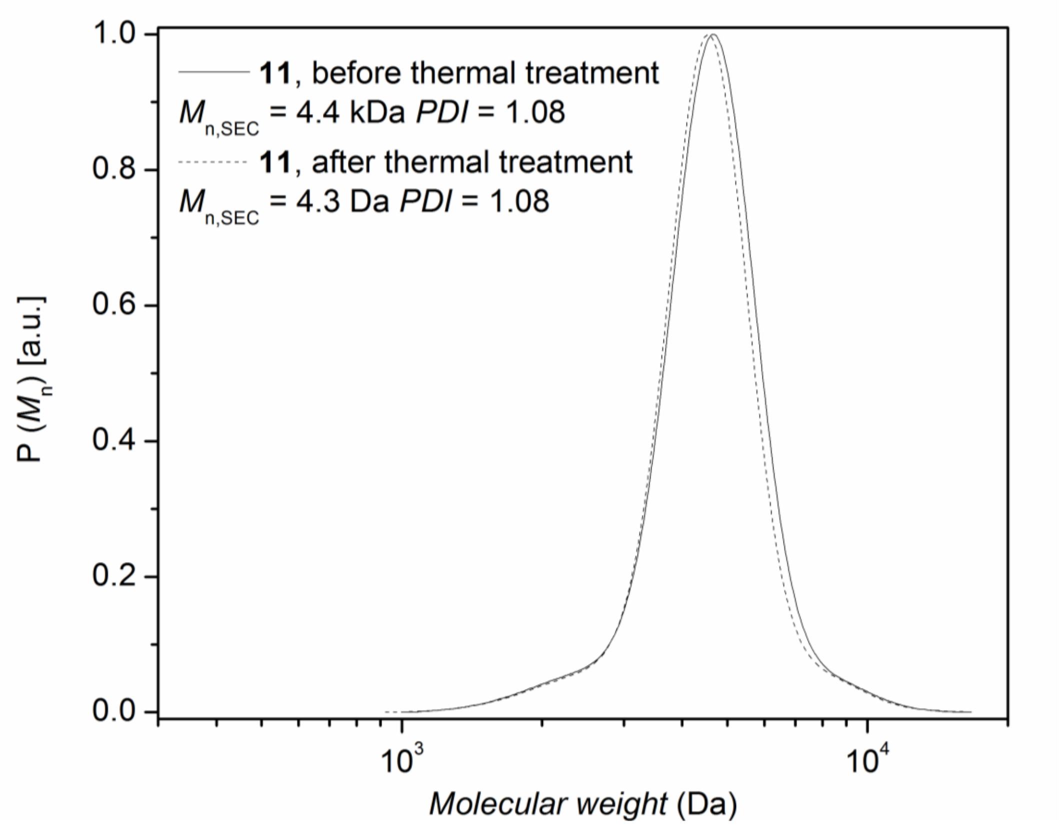


Figure S11. SEC traces of polystyrene **11** before and after thermal treatment at 200 °C for 24 h in an argon atmosphere.

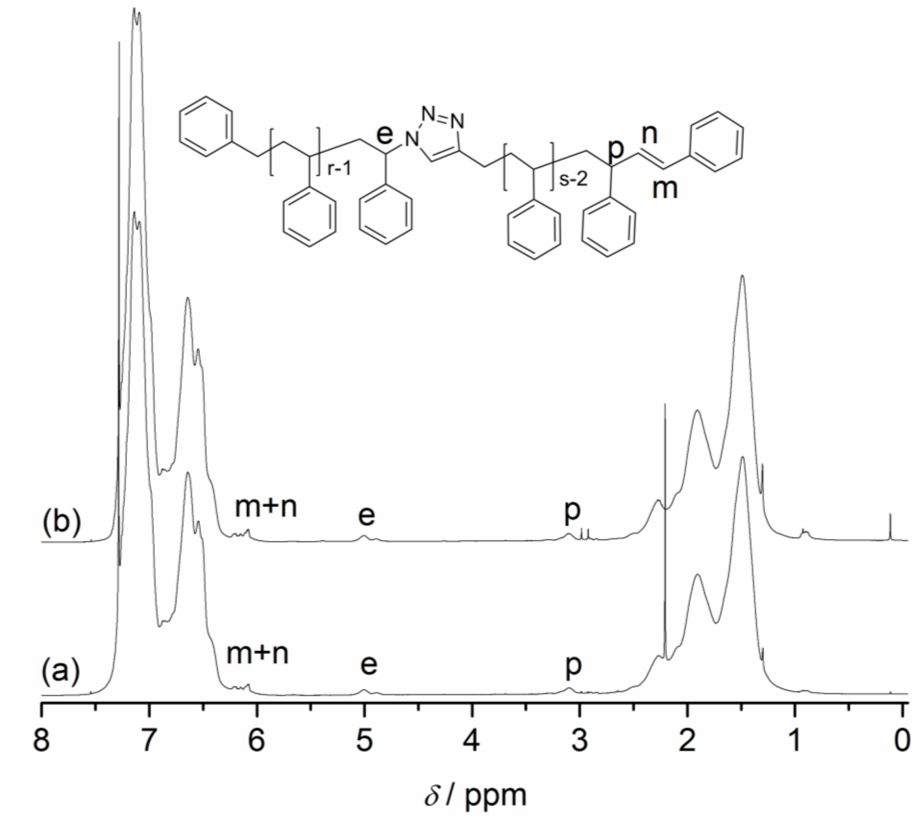


Figure S12. ^{1}H NMR spectra of polystyrene (**11**) recorded in $CDCl_3$ at ambient temperature: (a) before thermal treatment and (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.

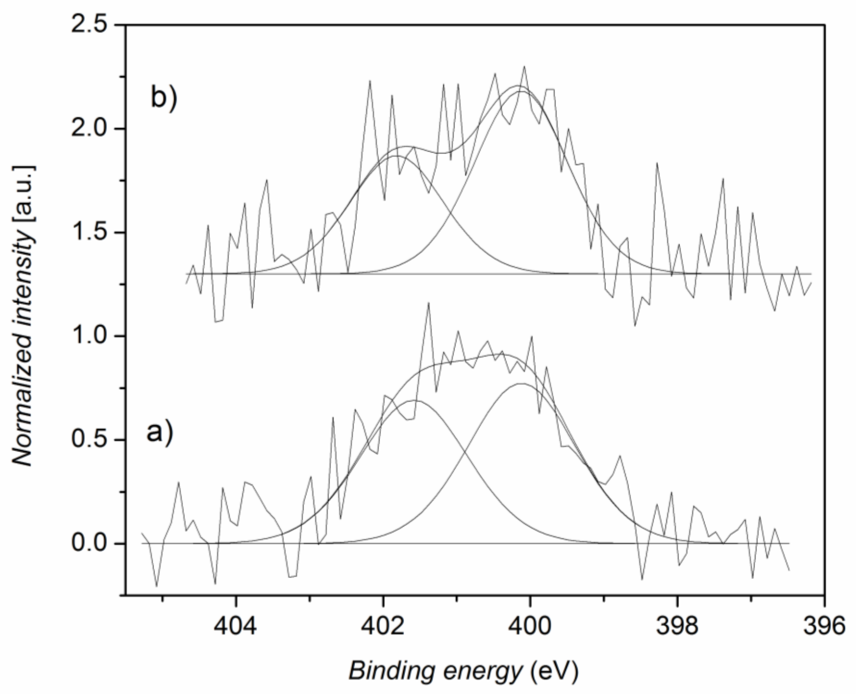


Figure 13. N 1s XPS spectra of polymer **11** before (**a**) and after (**b**) thermal treatment at 200 °C for 24 h in an argon atmosphere.

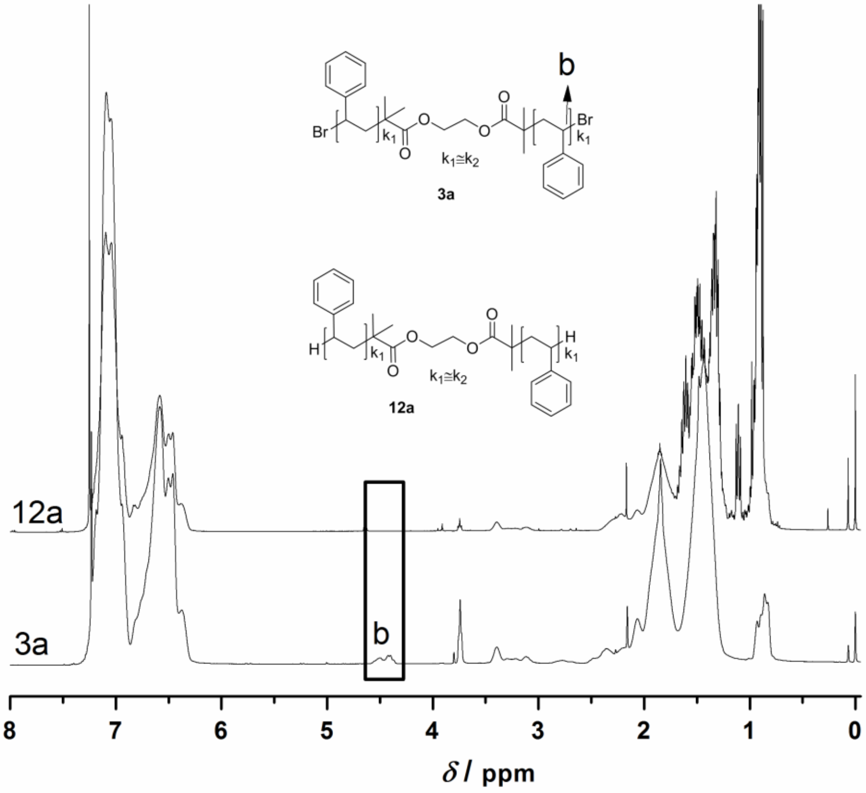


Figure S14. ^{1}H NMR spectra of polymer (**3a**) before treatment with Bu_3SnH and polymer (**12a**) after treatment with Bu_3SnH recorded in $CDCl_3$ at ambient temperature.

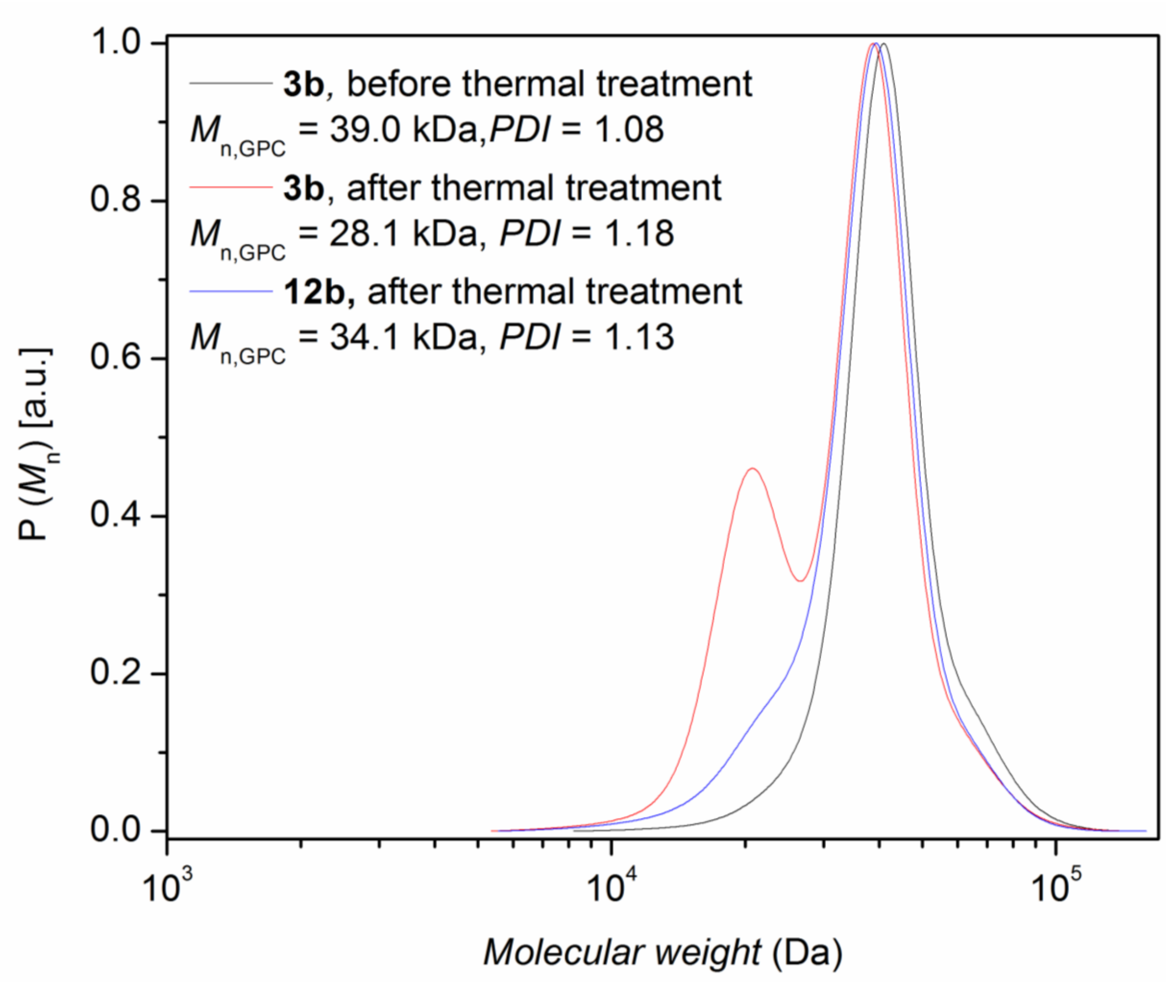


Figure S15. SEC traces of polystyrene **3b** before thermal treatment as well as polystyrene **3b** and polystyrene **12b** after thermal treatment at 200 °C for 24 h in an argon atmosphere.

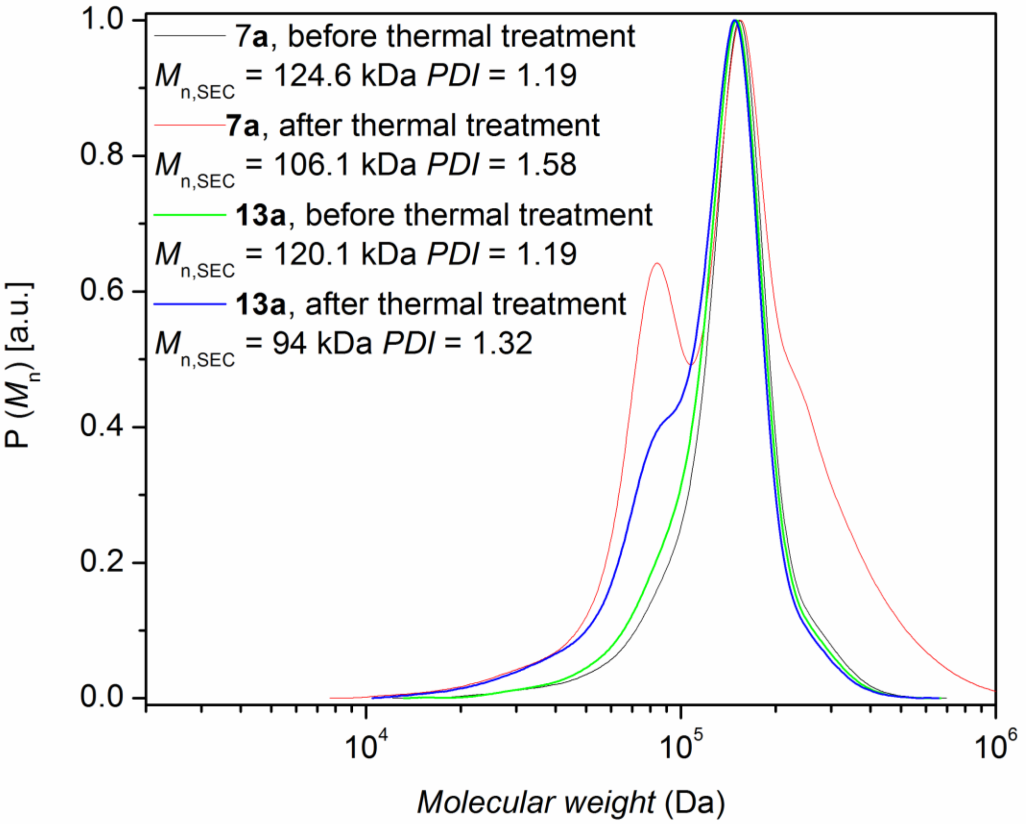


Figure S16. SEC traces of polystyrene **7a** and **13a** before thermal treatment as well as polystyrene **7a** and **13a** after thermal treatment at 200 °C for 24 h in an argon atmosphere.

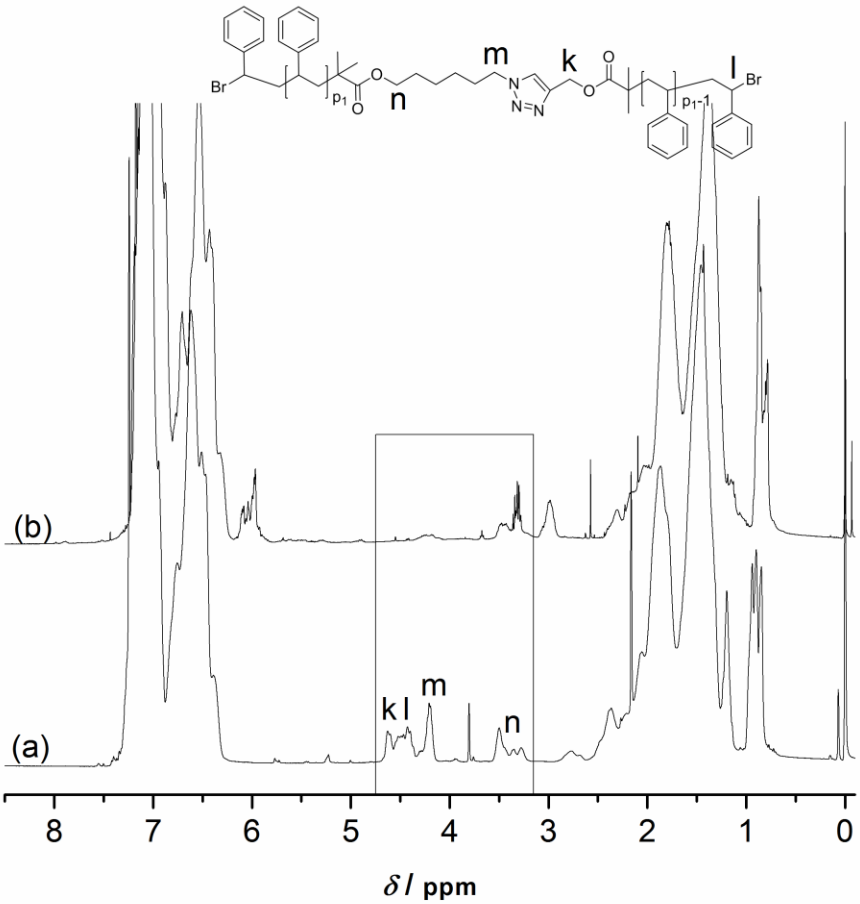


Figure S17. ^{1}H NMR spectra of polymer (**7b**) recorded in $CDCl_3$ at ambient temperature: (a) before thermal treatment and (b) after thermal treatment at 200 °C for 24 h in an argon atmosphere.

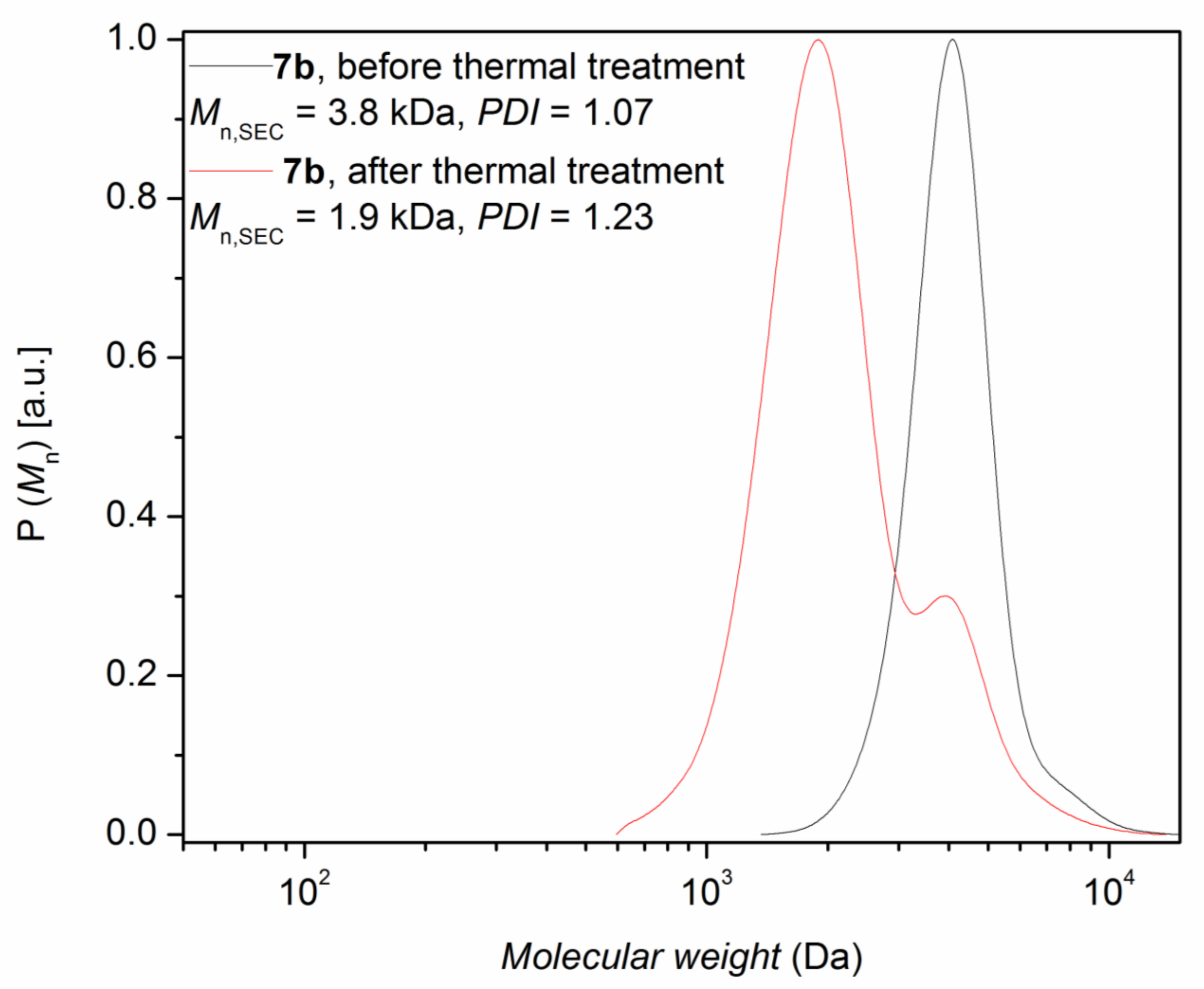


Figure S18. SEC traces of polystyrene **7b** before thermal treatment and after thermal treatment at 200 °C for 24 h in an argon atmosphere.

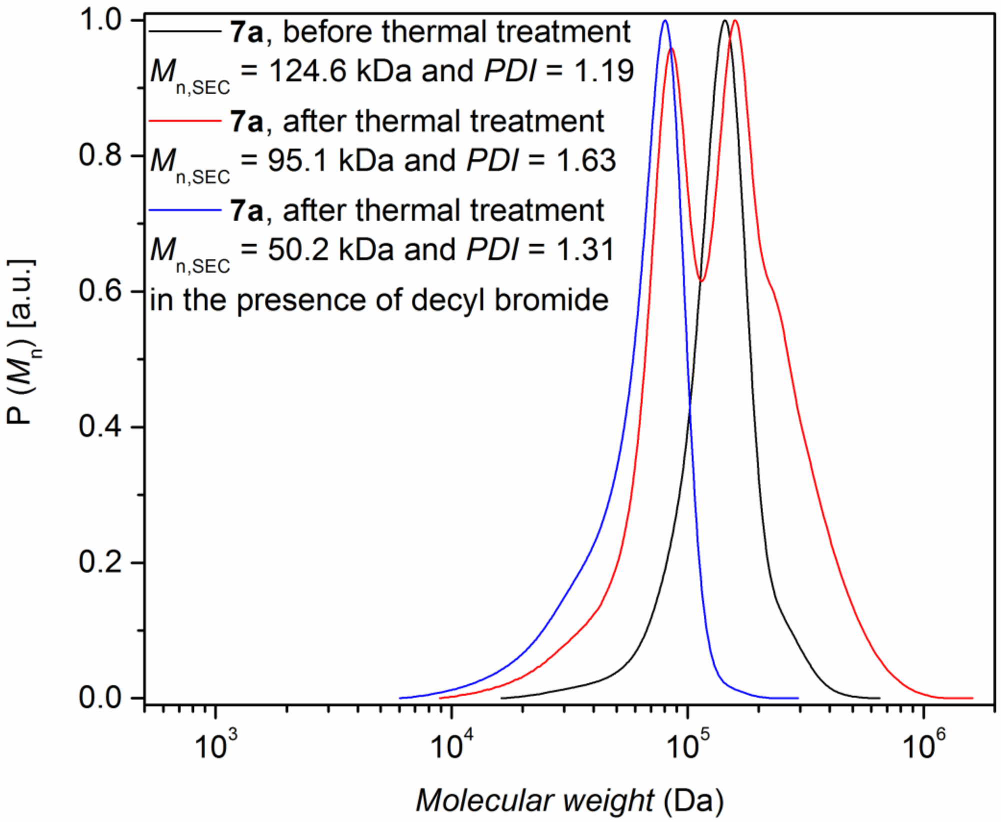


Figure S19. SEC traces of polystyrene **7a** before thermal treatment, after thermal treatment and after thermal treatment in the presence of decyl bromide at 200 °C for 24 h in an argon atmosphere.

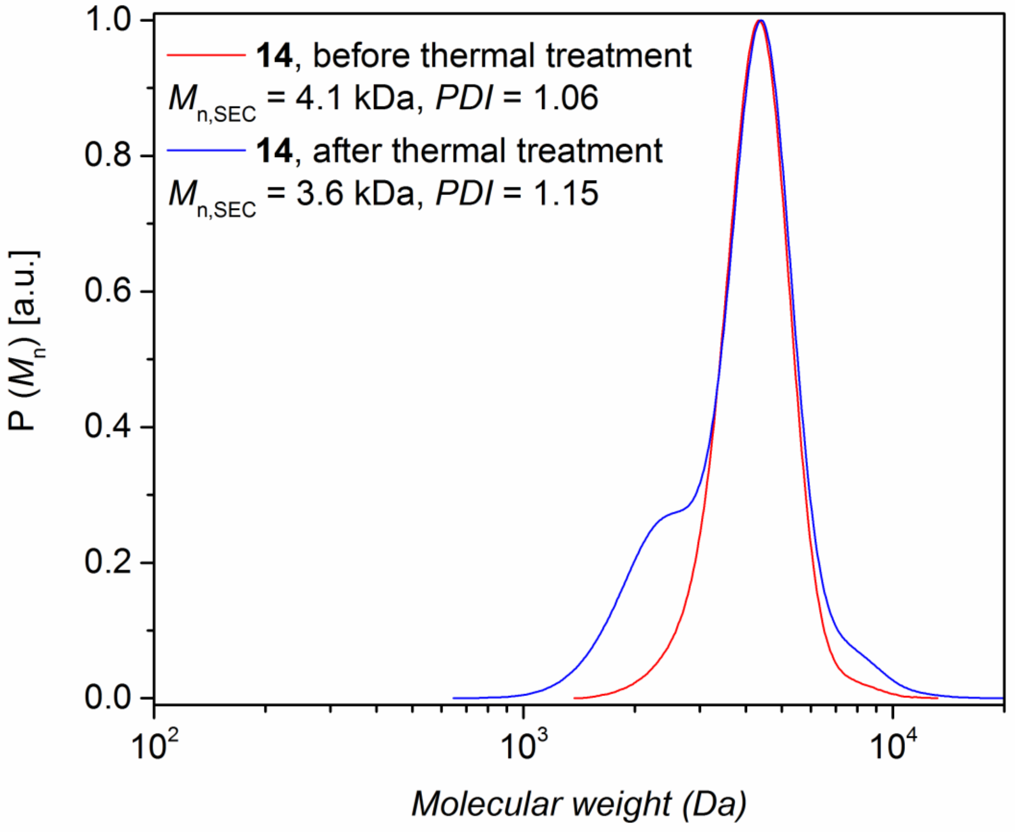


Figure S20. SEC traces of polystyrene **14** before thermal treatment and polysytrene **14** after thermal treatment at 200 °C for 24 h in an argon atmosphere.

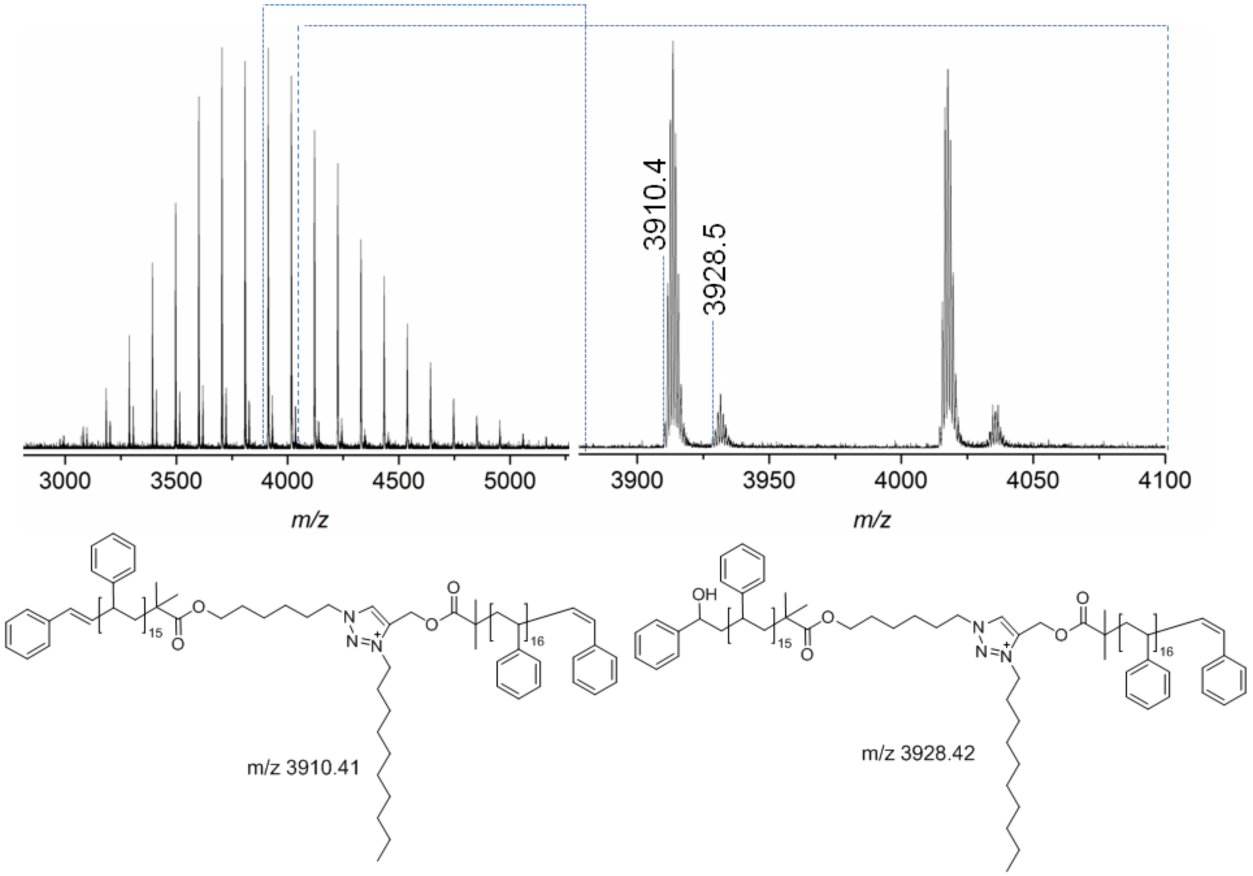


Figure S21. MALDI-MS spectra of polystyrene **14**. The observation of small signals at 18 mass units higher, i.e. *m/z* 3928.52, confirms the presence of the halide before MALDI analysis (refer to Scheme 3 and Scheme S1 for mechanistic details as well as Figure 9).

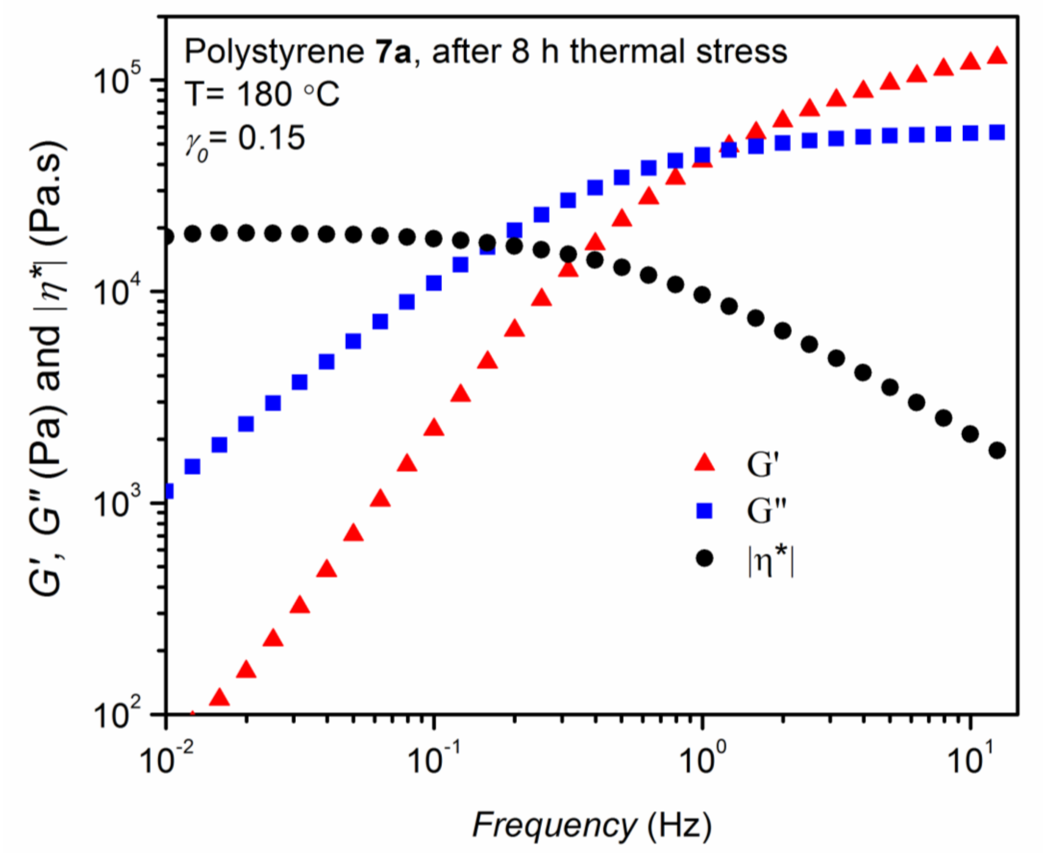


Figure S22. The absolute value of the complex viscosity and storage (G') and loss modulus (G'') as a function of frequency at 180 °C for polystyrene **7a** after an 24 hours time sweep test at a frequency of $\omega_1/2\pi$ = 0.05 Hz and 15% strain amplitude in a nitrogen atmosphere.

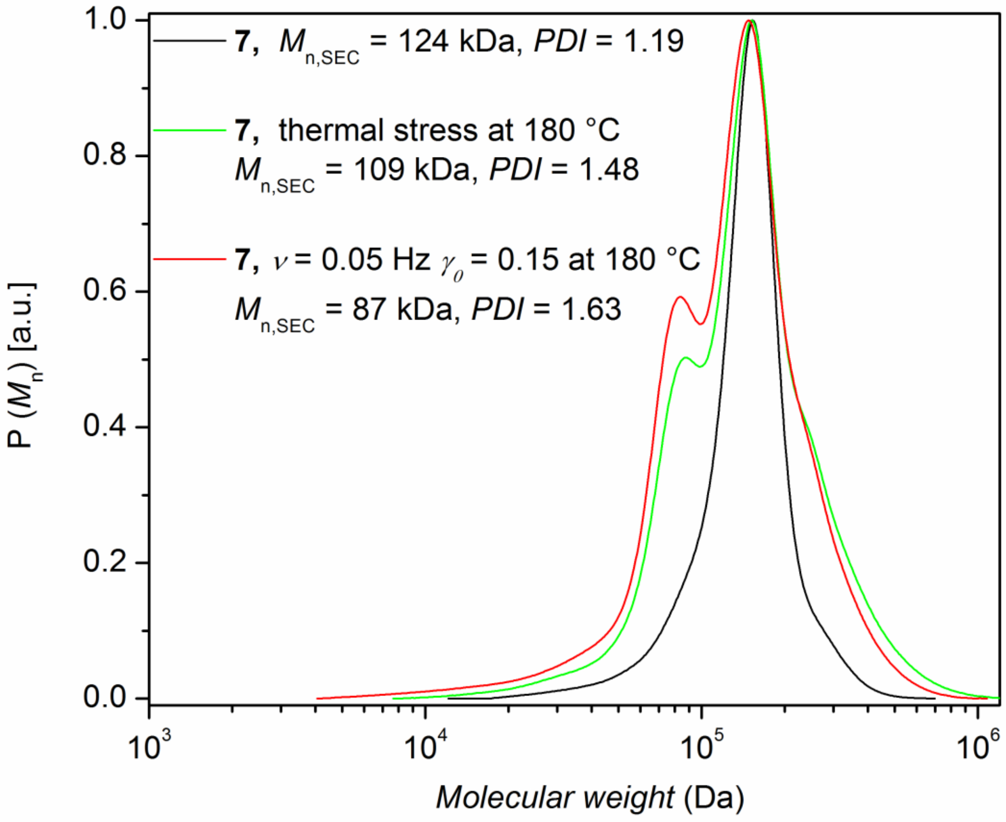


Figure S23. Comparison of number-average molecular weights of polymer **7a** at a mechanical excitation at a frequency of $\nu =$ = 0.05 Hz in a nitrogen atmosphere with 15% strain amplitude at 180 °C. SEC traces were taken after 24 h of thermal and thermomechanical stress.

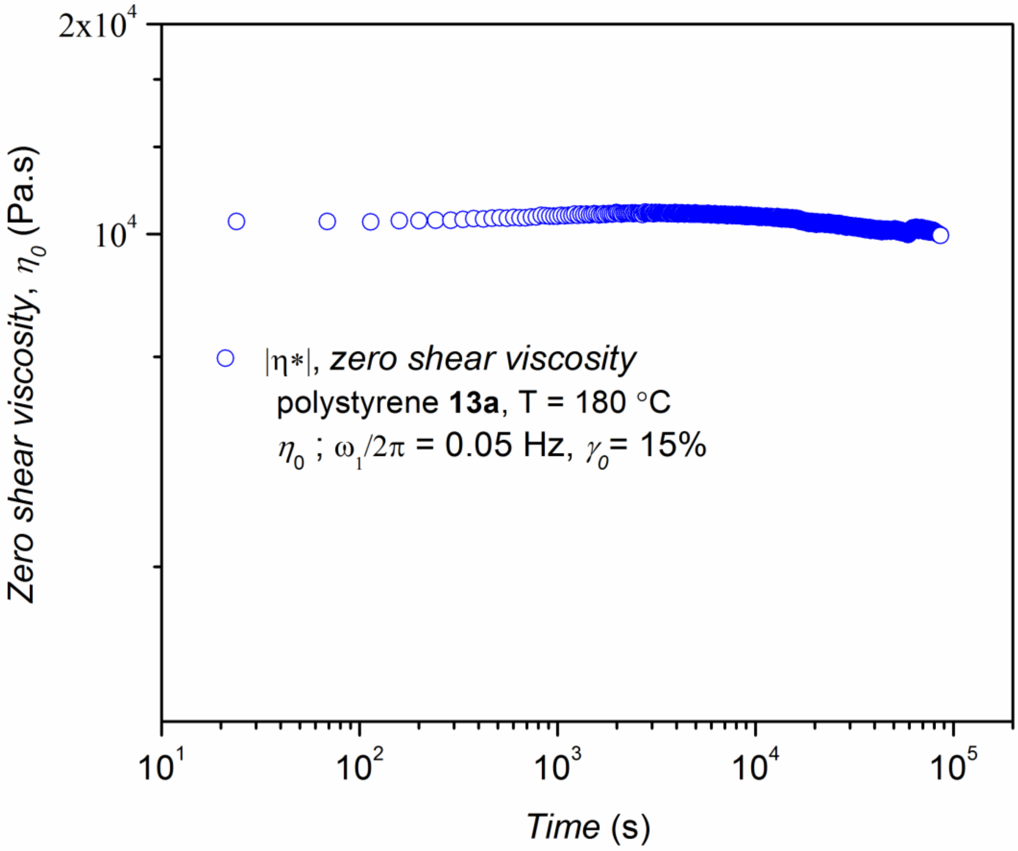


Figure S24. Time dependence of the experimental zero shear viscosity, specifically the absolute value of the complex viscosity of the polystyrene **13a**, as a function of time at 180 °C at a frequency of $\omega_1/2\pi = 0.05$ Hz and 15% strain amplitude in a nitrogen atmosphere.

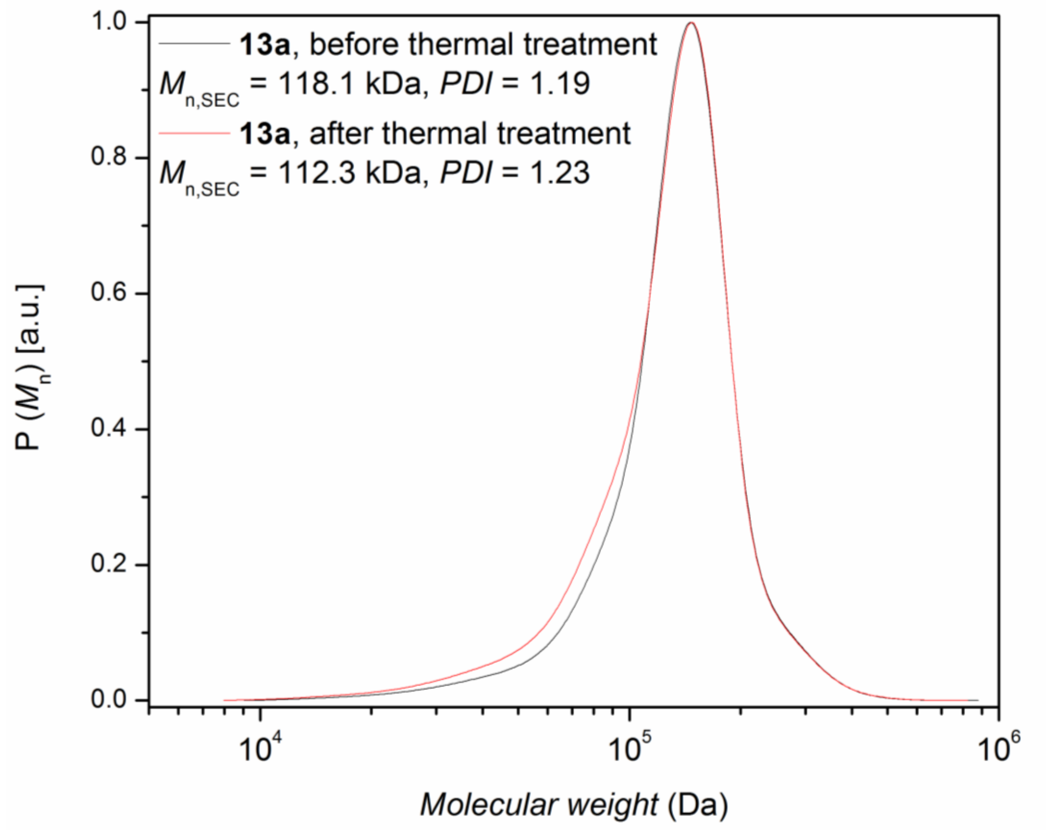


Figure S25. SEC traces of polystyrene **13a** before thermal treatment and after thermal treatment at 200 °C for 24 h in an argon atmosphere.

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