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Multi-Block Polyurethanes via RAFT End-group Switching and their Characterization by Advanced Hyphenated Techniques

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Abstract: The detailed characterization of poly(styrene)-*b*-poly(tetrahydrofuran) (pS-*b*-pTHF) multi-block copolymers ($17800 \text{ g mol}^{-1} \leq M_n \leq 46800 \text{ g mol}^{-1}$) generated via urethane linkages is presented. The synthesis of the block copolymers is enabled via a mechanistic switch of the thiocarbonyl thio end group of a poly(styrene) to dihydroxyl terminated polymers that subsequently react with a diisocyanate terminated

polytetrahydrofuran based prepolymer to form multi-block copolymer structures. The characterization of the multi-block copolymers and their substructures includes size exclusion chromatography (SEC), liquid chromatography at critical conditions (LCCC), nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy as well as matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. To obtain even further details of the polymer size and its composition, SEC with triple detection as well as newly developed SEC coupled online to IR spectroscopy was carried out. The quantification of the average block fractions via on-line SEC-IR (41 - 61 mol% pTHF) is in very good agreement with the results obtained via NMR spectroscopy (39 - 66 mol% pTHF).

Keywords: Polyurethanes; Multi-Block Copolymers; Liquid Chromatography at Critical Conditions LCCC; Soft Ionization Mass Spectrometry (ESI, MALDI); Size Exclusion Chromatography Coupled to Infrared Spectroscopy; Reversible Addition Fragmentation Chain Transfer (RAFT); End Group Transformation.

Introduction

The key driving force of synthetic polymer chemistry is the generation of complex and tailor-made functional polymer architectures such as block copolymers. Due to their high variability during synthesis and their resulting microstructure, block copolymers are applied in various fields ranging from microelectronics to drug delivery.^{1,2} In recent years controlled/living radical polymerization such as nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer polymerization (RAFT) gained high significance for block copolymer synthesis due to their ability of producing

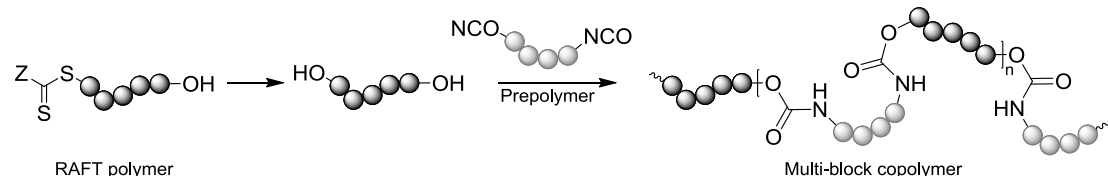
polymers with low polydispersity and high chain-end functionality.³ The block copolymer formation can then be performed either via the reaction of two polymer chains with specific end-functionalities (modular ligation) or via chain extension at the dormant end functionality.⁴

For the formation of multi-block copolymers, the same requirements exist as for diblock copolymers, however, the polymer chains should not only possess one, but two end functionalities. There exists a variety of multi-block copolymer synthetic strategies. A powerful approach proceeds via sequential anionic polymerization.⁵ An alternative route is via controlled/living radical polymerization such as ATRP and RAFT.⁶ Modular ligation concepts can be applied as an alternative method to synthesize well defined multi-block copolymers.⁷ Examples of combining different polymerization techniques to form multi-block copolymers can also be found in the literature. For example, Mahanthappa and coworkers synthesized multi-block copolymers via a combination of ring-opening metathesis polymerization (ROMP) and NMP.⁸ The sequential method of ring-opening polymerization and polycondensation also leads to multi-block copolymer formation.⁹

Polyurethanes (pU) find – due to their flexible construction options – a wide variety of applications such as tissue engineering, coatings and adhesives.¹⁰ Linear polyurethanes are commonly synthesized via polyaddition reactions of a diol and a diisocyanate.¹¹ Due to the rigidity and H-bonding of the urethane linkages, the polyurethane chains precipitate in many solvents and become insoluble with increasing chain length. Thus, macromolecular diols are often inserted in the polyaddition process to obtain a higher chain mobility and thus solubility of the polymer chains.¹²

The combination of polyurethane chemistry and multi-block copolymer structures can result in new material properties and applications. Yin *et al.* reported that an improvement of the material properties – including mechanical properties and water resistance – are obtained by the insertion of vinyl polymers into the polyurethane structure.¹³ Potential shape memory materials were generated via a pU-multi-block synthesis by several groups.¹⁴ A synthetic strategy entailing RAFT, ROP and polyurethane chemistry was realized by Webster and coworkers for coating films.¹⁵

In recent publications we presented a procedure to modify the thiocarbonyl thio end group of RAFT polymers into a hydroxyl moiety.¹⁶ This transformation process opens the unique possibility to employ RAFT-made polymers as building blocks – provided they feature two hydroxyl functionalities – for the construction of polyurethanes as macromonomers. We have employed the thiocarbonyl thio to hydroxyl-function switch in previous studies that focused on the preparation of block copolymers structures prepared via RAFT and ring-opening polymerization.¹⁷ In Scheme 1 the general synthetic strategy followed in the current contribution is depicted.



Scheme 1 Schematic overview of the mechanistic switch from RAFT polymerization via end group modification into dihydroxyl terminated polymers which enables a polyaddition with isocyanate-based prepolymers for the formation of multi-block copolymers.

The molar mass and the structure of linear polyurethanes and multi-block copolymers are conventionally characterized via NMR, FT-IR and SEC, presuming the material is soluble in suitable solvents.¹⁸ The determination of the molar masses of multi-block copolymers featuring building blocks which vary highly in their chemical composition is inaccurate when assessed via conventional SEC due to the absence of accurate calibration methods. For obtaining more exact molecular weight values of the copolymers, size exclusion chromatography coupled to triple detection can be applied.¹⁹ With triple detection – a sequence of differential refractive index detector, differential viscometer and especially multi-angle light scattering detector – the absolute molecular weight of complex polymers can be determined.

A very elegant way to obtain information of the chemical structure of a sample as a function of its molar mass is size exclusion chromatography coupled online to electrospray ionization mass spectrometry (ESI-MS) and nuclear magnetic resonance detectors.²⁰ However, ESI-MS is limited to relatively small macromolecules ($m/z \leq 2000$) while nuclear magnetic resonance detectors are cost-intensive and the SEC coupling is – due to solvent issues – not straight-forward. SEC coupled to Fourier transform infrared spectroscopy is rarely used and in general proceeds off-line. The eluent of the SEC system is sprayed on an interface and the solvent is evaporated. Subsequently, the germanium circle plate – serving as target – is positioned in an FT-IR device for detection.²¹ The off-line SEC/FT-IR assembly requires a high sample mass or long scanning time to obtain spectra with a good resolution, which results in elongation of the analysis time. Furthermore, quantification of individual components can be challenging due to crystallization or oxidation of the analyte during the deposition process.²² Existing on-flow systems are for several reasons restricted to high temperature SEC for polyolefines in

trichlorobenzene²³ or by the use of deuterated water as eluent in the protein analysis.²⁴ They are not transferable to conventional SEC solvents and conditions used for general polymer characterization. In here, a new SEC/FT-IR coupling method is utilized for the detection of the multi-block copolymers circumventing these problems with the aid of specialized mathematical solvent suppression techniques. This coupled measuring technique is being currently developed; the fundamental concept and first results have been reported in reference.²⁵

In the current contribution the synthesis of multi-block urethane-based copolymers via RAFT end-group switching and the subsequent characterization with state-of-the-art hyphenated methods are demonstrated.

Experimental Section

Materials

Styrene (99% extra pure, stabilized, Acros Organics) was purified by percolating through a column of basic alumina prior to use. 2,2'-Azobis(isobutyronitrile) (98%, Sigma Aldrich) was recrystallized twice from ethanol prior to use. Triphenylphosphine (PPh₃, Merck), tetrahydrofuran (multisolvant, 250 ppm BHT, Scharlau), tetrahydrofuran (HPLC grade, inhibitor-free, Bernd Kraft GmbH), 2,2,4-trimethylhexane-1,6-diisocyanate (TMDI, Evonik), poly(tetrahydro-furan) ($M_n \sim 1000 \text{ g mol}^{-1}$, Sigma Aldrich), 2[(dodecylsulfanyl) carbonothioyl]-sulfanyl propanoic acid (DoPAT, Orica Pty Ltd., Melbourne, Australia), propanediol (Sigma Aldrich), di-*n*-butyltindilaurate (DBTDL, Alfa Aesar), 4-dimethylamino pyridine (DMAP, ABCR), *N,N'*-dicyclohexylcarbodiimide (DCC, Alfa Aesar) and *N,N'*-dimethylacetamide (DMAc, Acros Organics) were used as received.

Synthesis of the RAFT Agent 3-Hydroxypropyl2-(((dodecylthio)carbonothioyl)thio)propanoate 1 (adapted from reference 26), see Scheme 2

The RAFT agent was synthesized via a Steglich esterification of the acid group of DoPAT. 6.33 g of DoPAT (18.1 mmol), 5.66 g of propanediol (74.4 mmol) and 0.45 g of DMAP (3.7 mmol) were dissolved in 40 mL of dry dichloromethane. A solution of *N,N'*-dicyclohexylcarbodiimide (5.70 g, 27.6 mmol) in dry methylene chloride (10 mL) was slowly added, the cooling bath was removed and the mixture was stirred overnight at ambient temperature. The white precipitate was filtered off and the solution was extracted with 0.5 N hydrochloric acid (2×50 mL) and washed with saturated NaHCO_3 solution (50 mL). The organic solution was dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified via column chromatography on silica gel with hexane/ethyl acetate (10 : 1, v/v, r_f 0.2) as the eluent and dried under high vacuum to yield the RAFT agent **1** (3.39 g, 46%) as a yellow solid. ^1H NMR (400MHz, CDCl_3) δ / ppm: 0.81 (t, 3H, $-\text{CH}_3$), 1.19 (m, 18H, $-\text{CH}_2$), 1.58 (d, 3H, $-\text{CH}_3$), 1.63 (m, 2H, $-\text{CH}_2$), 1.82 (m, 2H, $-\text{CH}_2$), 3.29 (t, 2H, $-\text{CH}_2\text{S}$), 3.63 (t, 2H, $-\text{OCH}_2$), 4.24 (m, 2H, $-\text{CH}_2\text{O}-$), 4.48 (q, 1H, $-\text{CH}$).

Preparation of the Thiocarbonyl Thio Terminal Polystyrene 2

A solution of RAFT agent (**1**) (0.888 g, 37.1 mmol L^{-1}) and 2,2'-azobis(isobutyronitrile) (40 mg, 2.4 mmol L^{-1}) in 100 mL styrene was freed from oxygen by purging with nitrogen for 20 min. The solution was heated to 60°C for 240 min. The reaction was stopped by cooling with liquid nitrogen and the polymer was precipitated in cold methanol. The average molar mass and the polydispersity was determined via SEC, calibrated with pS standards. ($M_n = 3900 \text{ g mol}^{-1}$, $PDI = 1.2$).

End-Group Switching (Synthesis of Species 3)²⁷

A solution of 2,2'-azobis(isobutyronitrile) (50 mmol L⁻¹) and the RAFT-polymer (**2**) (1.5 mmol·L⁻¹ based on its M_n) in THF was heated to 60 °C under vigorous stirring. After 40 min, the temperature was reduced to 40 °C and 3 equiv. triphenylphosphine were added. After 20 min the solution was concentrated under reduced pressure with subsequent precipitation of the polymer in cold methanol. The molar mass was determined with SEC, calibrated with pS standards ($M_n = 3700 \text{ g mol}^{-1}$, $PDI = 1.1$). The MALDI-TOF spectrum of **3** can be found in Figure 1.

Table 1 Assignment of the theoretical and measured m/z ratios of OH-pS-OH with 24 repeat units (see the Figure 1).

Structure	[M + K] ⁺		
	m/z^{theo}	m/z^{exp}	$\Delta m/z$
OH-pS-OH	2648.41	2648.66	0.25

Synthesis of the Prepolymer (Synthesis of Species 4)²⁸

0.28 g of pTHF (~1000 g·mol⁻¹), dissolved in dry DMAc, were added to a solution of 0.089 g TMDI and 0.02 g of DBTDL in DMAc at 80 °C under a nitrogen atmosphere. The mixture was stirred for 3 h. The prepolymer was dried for 5 h under reduced pressure at 100 °C. The SEC traces of pTHF and the prepolymer can be found in Figure S1 in the Supporting Information section. However, due to the inaccuracy of the SEC analysis, for the molar masses of the prepolymer a value of close to 2500 g·mol⁻¹ is assumed, given by the addition of 3 isocyanate molecules and 2 pTHF chains.

Synthesis of the Multi-Block Copolymers Poly(styrene)-b-poly(tetrahydrofuran)
(*Synthesis of Species 5-9*)

The obtained prepolymer (PP) **4**, dissolved in 1 mL DMAc, was heated to 80 °C under a nitrogen atmosphere. A solution of 0.414 g dihydroxy-terminated polystyrene **3** in DMAc (1.5 mL) was added to 0.02 g of di-*n*-butyltin dilaurate. The mixture was stirred for 48 h. The solution was cooled to stop the reaction and precipitated in methanol. The amount of pS was varied according to the required equivalents (see Table 2).

Table 2 Reaction conditions for the polyaddition as well as number average molar masses, M_n , and polydispersity indices, PDI s, of the poly(styrene)-*b*-poly(tetrahydrofuran) multi-block polyurethanes.

Structure	Equivalents prepolymer:pS	m (PP) / g	m (pS) / g	M_n / g mol ⁻¹	PDI
5	1:1.5	0.14	0.31	10300	2.1
6	1:1	0.28	0.41	14000	2.5
7	1.5:1	0.08	0.08	23000	2.9
8	2:1	0.12	0.08	30500	3.0
9	2:1	0.12	0.08	27800	2.6

Size Exclusion Chromatography (SEC)

For the determination of molecular mass distributions (MMD), an SEC system (Polymer Laboratories PL-GPC 50 Plus) comprising an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm) followed by three linear columns (PLgel Mixed C,

300 × 7.5 mm, 5 µm bead-size) and a differential refractive index detector was employed. THF was used as the eluent with a flow rate of 1 mL·min⁻¹, the column temperature was set to 40 °C. The SEC system was calibrated using narrow poly(styrene) standards ranging from 160 to 6·10⁶ g·mol⁻¹ (Polymer Standard Service GmbH, Mainz). The resulting molar mass distributions were reassessed by universal calibration using Mark-Houwink parameters for poly(styrene) ($K = 14.1 \cdot 10^{-5} \text{ dL g}^{-1}$ and $\alpha = 0.70$).²⁹ For the multi-block copolymers, the Mark-Houwink parameters for poly(styrene) were employed.

Liquid Chromatography under Critical Conditions (LCCC): The measurements were carried out on a Hewlett Packard (HP1090) HPLC system using a diode array UV detector and an evaporative light scattering detector (ELSD, Sedere, France). The flow rate was 0.5 mL min⁻¹; 25 µL of close to 2 wt.% polymer solutions were injected. For the critical conditions of polystyrene a reversed phase system was employed: A YMC-ODSA column (250 × 3 mm inner diameter) with 300 Å pore size and 5 µm average particle size. The eluent was a mixture of tetrahydrofuran and water. The critical solvent compositions for poly(styrene) contain 88.4 % (v/v) THF.

Size Exclusion Chromatography (SEC) with Triple Detection The triple-detection chromatographic setup used for the determination of the exact molar mass of the multi-block copolymers consisted of a modular system (Polymer Standard Service, PSS, Mainz/Agilent 1200 series) incorporating an ETA2010 viscometer (WGE Dr. Bures) and a multi-angle light-scattering unit (PSS SLD7000/BI-MwA, Brookhaven Instruments). Sample separation is achieved via two linear columns provided by PSS (SDVLux-1000 Å and 10⁵ Å, 5 µm) with THF as the eluent at 35 °C with a flow rate

of 1 mL min^{-1} . The exact M_w is determined by measuring the light scattering at an angle of 90° and utilizing the method ‘factor multiplied with concentration’ for data analysis. The factor for the concentration detector was determined by measuring a narrow dispersed polystyrene standard of $120\,000 \text{ g}\cdot\text{mol}^{-1}$ of a known concentration.

Size Exclusion Chromatography (SEC) Coupled to a Fraction Collector

For fractionation of polymer samples, an SEC system equipped with a high speed column (SDV, linear M) was connected to a fraction collector (Super Fraction Collector CHF122SC, Advantec, Japan). The concentration of the samples was 10 g L^{-1} . At a flow rate of 1 mL min^{-1} fractions were collected every 20 s. Fractionation was repeated 10 times. The fractions from 6.65-9.95 mL were combined and dried for further analysis.

Size Exclusion Chromatography (SEC) Coupled to Infrared Spectroscopy (FT-IR)

For the detection of the SEC elugrams via online IR spectroscopy, a modular system (Polymer Standard Service, PSS, Mainz/Agilent 1200 series) was coupled to a Vertex 70 FT-IR spectrometer (Bruker Optics, Ettlingen). A SDV semi-preparative column linear M (PSS) was utilized for the separation of the samples. A concentration of $10\text{--}15 \text{ g L}^{-1}$ was prepared for the injected volume ($100 \mu\text{L}$) of the samples. The sample cell of the IR spectroscopy was a self-designed flow-cell, based on a six reflexions ATR unit (Gateway, Specac, Cranston, RI, USA). The eluent was THF, the flow rate 1 mL min^{-1} . IR spectra were taken every 5 seconds and 50 scans were co-added. Further mathematical solvent suppression and data treatment were performed with an in-house written MATLAB routine.²⁵

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H-NMR spectroscopy was carried out on a Bruker AM 400 MHz as well as a Bruker AM 250 MHz spectrometer. All samples were dissolved in CDCl₃. The δ -scale is indirectly referenced to the signal of CHCl₃.

MALDI-TOF Mass Spectrometry

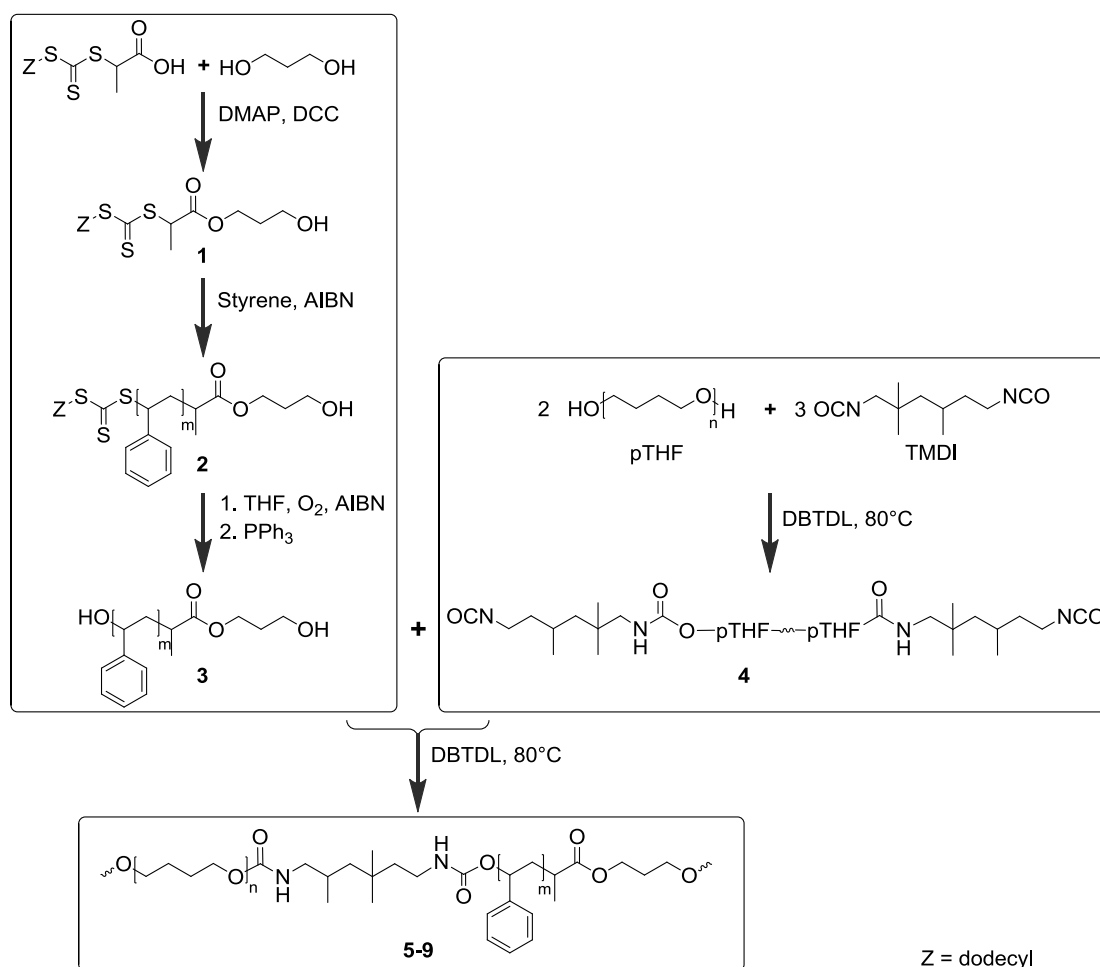
An Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) was utilized. The system was equipped with a Smartbeam laser ($\lambda = 356$ nm). 2000 laser shots were accumulated for one spectrum. Dithranole (THAC) and 2-[(2 E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) (10 mg mL⁻¹ in THF) were used as matrix. Typically, 2 μ L of a silver trifluoroacetate (AgTFAc) solution ($c = 2$ mg mL⁻¹) were added for the ionization of poly(styrene). For sample preparation, a volume of 20 μ L of polymer solution was mixed with 50 μ L of matrix solution; subsequently, 1 μ L was deposited on the MALDI target using an Eppendorf pipette.

Results and Discussion

Previously, we reported the synthesis and the advanced characterization of pS-*b*-pCL di-, tri- (and star) block copolymers based on a mechanistic switch from RAFT to ROP via a modification of the thiocarbonyl thio group to an OH end functionality.¹⁷ In here, the modification of the thiocarbonyl thio moiety to an OH group is carried out to connect the poly(styrene) chains to a diisocyanate terminated prepolymer to afford multi-block copolymers consisting of poly(styrene) and poly(tetrahydrofuran) units via urethane linkages. To obtain multi-block copolymers, difunctional building blocks

are required. For this purpose, the RAFT agent 2[(dodecylsulfanyl) carbonothioyl]sulfanyl propanoic acid (DoPAT) was esterified in the first step with 1,3-propanediol (see Scheme 2, **1**) via a Steglich esterification employing *N,N'*-dicyclohexylcarbodiimide (DCC) as a coupling agent. After the polymerization of styrene **2** via the RAFT process, the thiocarbonyl thio moiety was modified to form the dihydroxy-terminated polymer **3**.

The multi-block copolymers **5-9** are subsequently obtained by a polyaddition of the diisocyanate end group containing prepolymer **4**, which was synthesized from poly(tetrahydrofuran) and 2,2,4-trimethylhexane-1,6-diisocyanate and the dihydroxy terminated polystyrene.



Scheme 2 Reaction sequence and conditions for the synthesis of the multi-block copolymers poly(styrene)-*b*-poly(tetrahydrofuran).

The diol end-functionalized polystyrene was characterized via SEC and MALDI-TOF MS. In Figure 1, the MALDI-TOF mass spectrum of the polystyrene with the two hydroxyl end moieties **3** is depicted. The inset shows the simulated isotopic pattern of OH-pS-OH in comparison to the measured data, which match perfectly. No starting material and no additional distributions were detected. The MALDI mass spectrum confirms that no other end groups are attached to the polymer chain and a quantitative thiocarbonyl thio to hydroxyl conversion is obtained.

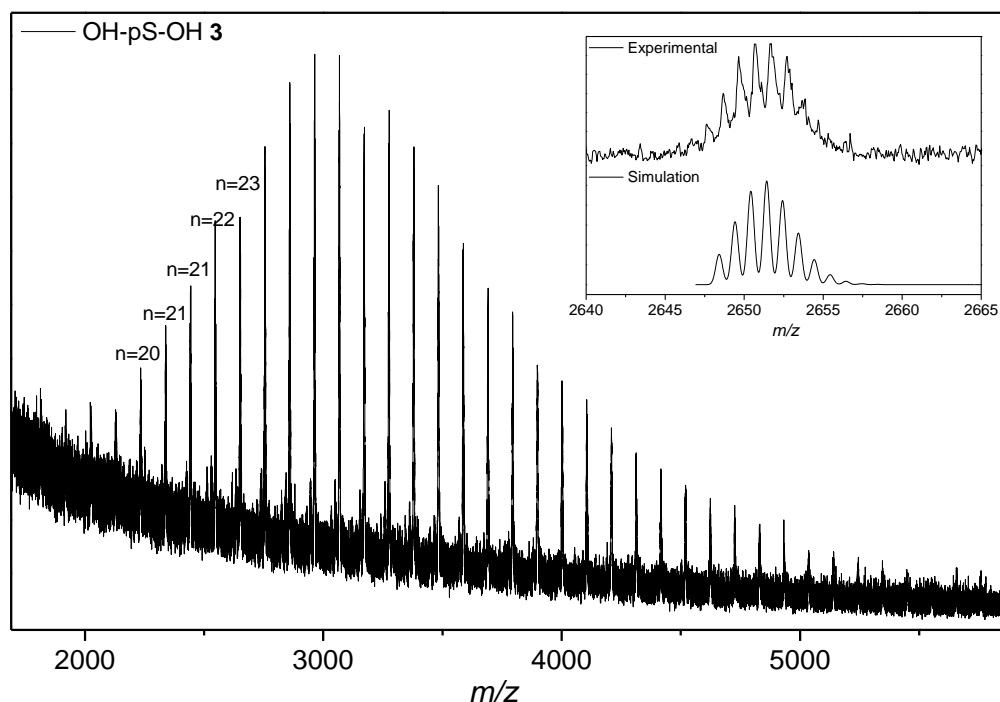


Figure 1 MALDI TOF mass spectrum of the dihydroxy-terminated poly(styrene) obtained via modification of the RAFT end group. The inset depicts the comparison of the measured spectra with the simulated isotopic pattern (Gaussian profile with 0.5 Dalton resolution of $[M+Ag]^+$).

Forming block copolymers via urethane linkages requires – beside the dihydroxy terminated polymer – a second polymer type featuring two isocyanate end groups. Due to solubility issues, poly(tetrahydrofuran) was chosen as a soft segment within the multi-block copolymer. The exact molecular weight ($M_n = 990 \text{ g mol}^{-1}$) of pTHF was determined by adding trichloro acetyl isocyanate to the NMR tube and subsequently integrating and comparing the signals of the end group with the signals of the polymer backbone. The pTHF was equipped with isocyanate end groups via a prepolymer synthesis. A pTHF to diisocyanate ratio of 2 to 3 was chosen to obtain a doubling in molecular weight.²⁸ The prepolymer was analyzed via SEC and the

isocyanate content was determined via titration. The SEC trace of the prepolymer, confirming the increase in molar mass, is presented in Figure S1 of the Supporting Information section and is compared with the SEC elugram of the initial pTHF.

In the last synthetic step the prepolymer and the diol terminated polystyrene were combined with the catalyst *i.e.*, di-*n*-butyltin dilaurate (DBTDL) and dissolved in DMAc. Via such an addition process, high molar masses can only be obtained if the exact stoichiometry of the components is adhered to. When employing macromolecules in the polyaddition process, generating accurate stoichiometry is hampered due to the polydisperse nature of the macromolecules. Consequently, the equivalents of the prepolymer NCO-pTHF-NCO compared to the OH-pS-OH were varied to obtain multi-block copolymers with high molar masses and with minor amounts of residual starting material. The multi-block copolymers were formed at a temperature of 80 °C. After the synthesis, the pS-*b*-pTHF copolymers **5-8** were precipitated in cold methanol, dried and characterized in the first instance via conventional SEC (pS calibration). The ratios and the molar masses obtained in this fashion are collated in Table 2. The SEC trace of the multi-block copolymer pS-*b*-pTHF **8**, in comparison to the elugrams of the starting materials, is presented in Figure 2, whereas the SEC elugrams of the other multi-block copolymers **5-7** can be found in Figure S2 in the Supporting Information section. In the elugrams a clear shift of the starting material to the generated multi-block copolymer is observed. The polydispersity of the obtained polymer is relatively high (*PDI* between 2 and 3), as expected for this polyaddition process. It should be noted that the starting material, *i.e.* the pTHF prepolymer, already possesses a relatively high *PDI* (1.4). In addition, a small fraction in the SEC traces at lower molar masses is visible, which indicates that a low amount of starting material did not react, increasing the overall *PDI*. It is very

likely that the small amount of low molar mass material is polystyrene homopolymer based on the fact that the multi-block copolymer was precipitated in methanol, in which pTHF with a low molar masses does not precipitate well (vide infra). Due to the broad mass distribution of the prepolymer and an unavoidable SEC error in the pS molar mass determination, the complete disappearance of the starting material pS in the SEC traces of the copolymers was not achieved. It is noted that less starting material remains when increasing the pTHF : pS ratio (see Figure S2 in the Supporting Information section). It is expected that a slightly higher and optimal pTHF to pS ratio would eventually afford a copolymer without any residual pS left. Nevertheless, as a high molar mass copolymer containing only a minor content of pS homopolymer could be obtained with 2 equivalents of pTHF relative to pS (sample **8**, Table 2), the molar ratio of pTHF to pS was not further increased.

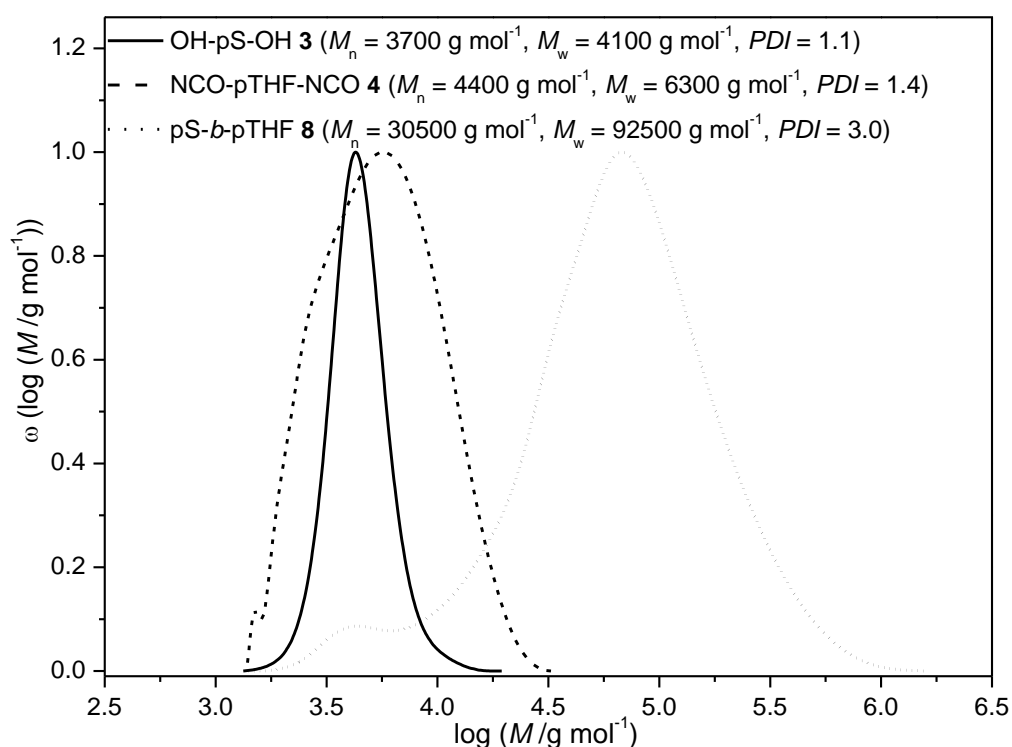


Figure 2 SEC trace of the multi-block copolymer sample **8** generated via urethane linkages. In addition, the SEC elugrams of the initial pS homopolymer and the pTHF

prepolymer are depicted. All molecular weight data given in the plot are based on a linear poly(styrene) calibration. For the synthetic approach and the chemical structures the reader is referred to Table 2 and Scheme 2, respectively.

With liquid chromatography under critical conditions, starting materials such as homopolymer residues in the multi-block copolymer samples can be identified. The critical conditions for polystyrene have been reported before.¹⁷ Under the same conditions, the multi-block copolymer sample **6** has been analyzed. The corresponding elugrams, in comparison to the polystyrene homopolymer, are depicted in Figure 3. In the evaporative light-scattering detector (ELSD) signal of sample **6** a small peak is observed at the same retention time where the homopolymer pS elutes. Thus, a first hint that pS homopolymer residue is present in the multi-block copolymer can be derived. To further clarify the nature of the side product, an additional UV detection at two different wavelengths (254 nm and 230 nm) has been applied. Polystyrene can absorb UV light readily and shows strong signals, whereas pTHF absorbs almost no UV light in THF. Furthermore, the molar absorptivity of polystyrene is higher in the region of shorter wavelengths. This circumstance was exploited to clearly identify the presence of homopolymer pS via the LCCC setup. Indeed, the elugrams in Figure 3 show that the small peak, which is visible by ELSD detection, is much more pronounced with UV detection at a wavelength of 254 nm and even more prominent at shorter wavelength (230 nm), thus verifying the assumption from the SEC traces that small pS homopolymer residues are present in the multi-block copolymer samples.

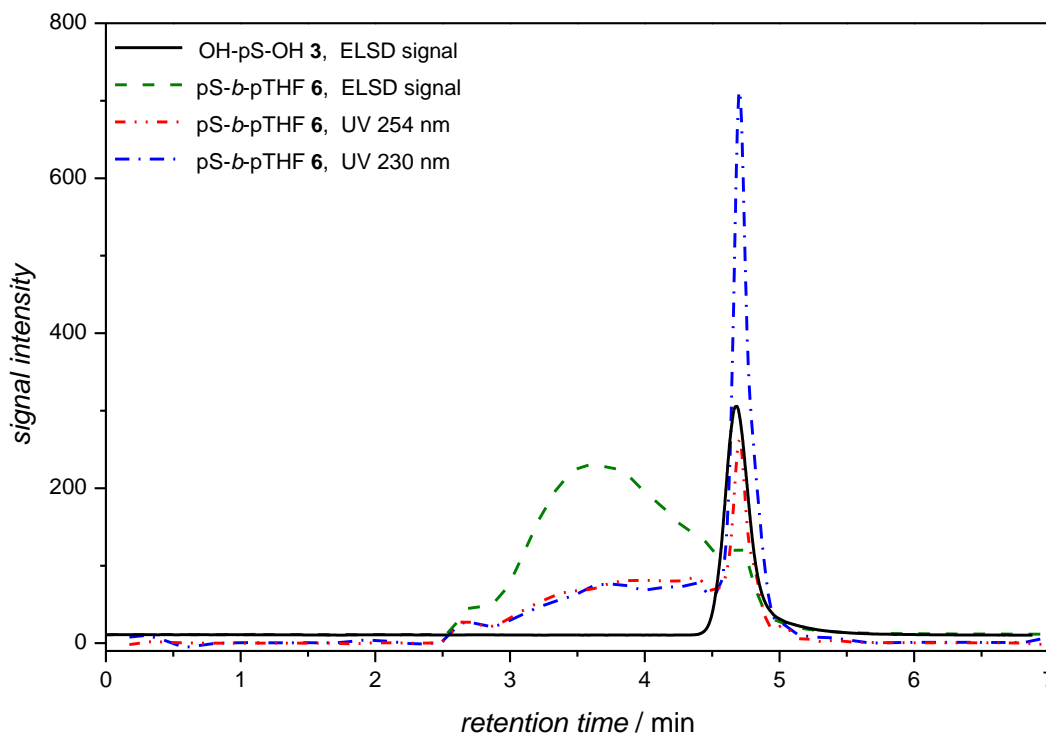


Figure 3 LCCC Elugrams of the multi-block copolymer sample **6** and the polystyrene precursor **3** at the critical conditions of polystyrene (YMC-ODSA column, 88.4 % THF / 11.6% H₂O (v/v)). The detection with UV at 254 nm and 230 nm is applied to reveal the polystyrene homopolymer content.

Conventional SEC is sufficient to obtain a first indication whether the synthesis was successful. However, it cannot determine the exact molar masses of the multi-block copolymers. Due to the very significant difference in polymer structure of poly(tetrahydrofuran) and poly(styrene) the molar masses determined via conventional SEC – which is calibrated via poly(styrene) standards – are beset with a substantial error. One way to determine accurate molecular weights of a polymer structure is by measuring the samples on a SEC system equipped with triple detection. The detection system combines viscosimetry, light-scattering and refractive index

detectors. Taking advantage of the fact that the excess Raleigh ratio is directly proportional to the product of the concentration and the weight-average molar mass M_w , the molecular weight can be determined directly by the combination of a concentration sensitive detector and the light scattering detector.³⁰ For an accurate detection of the molecular weights of the multi-block copolymers it is required that no homopolymer is present in the sample. One possibility would be to perform dialysis with an appropriate membrane. Yet, in here fractionation of the samples via a SEC system coupled to a fraction collector was employed. The conditions under which the separation proceeded can be found in the Experimental section.

After drying the fractionated samples, SEC with triple detection was performed. In Figure 4 and in Figure S3 of the Supporting Information section, the elugrams of the multi-block copolymer samples, obtained via SEC with triple detection, are presented. The molar masses and the PDI 's, which are obtained by a light-scattering detector, are included in the graphs. The elugrams reveal that the fractionation was successful as no shoulder or additional signal is detected in the lower molar mass region. Depending on the conditions used for the block copolymer synthesis, M_w varies between 26300 and 85700 g mol⁻¹. Due to the fractionation process, the dispersity indices decrease to values lower than two. If the dn/dc of homopolymers or polymers with homogeneous composition was determined before, the triple detection should allow obtaining accurate weight-average molecular weights.³¹ For multi-block copolymers, however, the dn/dc varies with the composition of the two blocks in the polymer. Thus, the dn/dc values are unemployable for multi-block copolymer samples with varying individual block content. Alternatively, the method “factor multiplied with concentration” can be applied for molecular weight determination as described in the Experimental section

giving the values shown in Figure 4 and Figure S3 of the Supporting Information section.

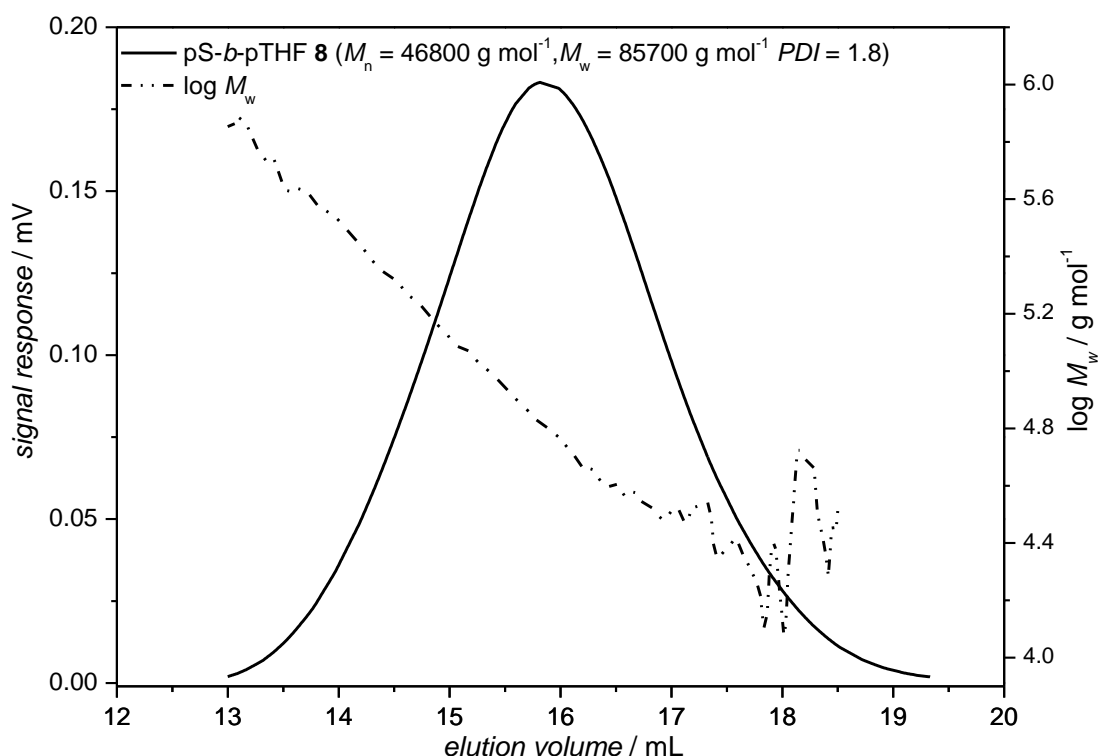


Figure 4 Molecular weight determination of the multi-block copolymer **8** after fractionation via SEC equipped with triple detection. From 18 mL elution volume onwards, the data are not considered due to the elevated scattering.

One important issue when considering utilizing the polymer as a potential material in the future is the accurate reproducibility of the polymerization process. Consequently, the synthesis accompanied with the characterization steps of the multi-block copolymer sample **8** was repeated, affording sample **9**. The SEC elugram, obtained via triple detection of the samples **8** and **9**, are compared in Figure S4. The determined molecular weights and the polydispersities are again included within the figure. Although the molecular weight of sample **9** ($M_w = 82400$ g mol⁻¹) does not match exactly with that of sample **8** ($M_w = 85700$ g mol⁻¹), the results are reproducible

within the accepted error margins of triple detection SEC ($\pm 15\%$).

While absolute SEC measurements provide the molecular weights of the samples, no information about the chemical composition is obtained. Due to the precipitation after the multi-block copolymer synthesis and the fractionation of the samples, it is very likely that the composition departs from the initial applied ratio between poly(styrene) and poly(tetrahydrofuran) in the synthesis. Therefore ^1H -NMR spectra of the samples **5-8** were recorded with a 400 MHz spectrometer in CDCl_3 . The NMR spectrum of sample **7** is depicted in Figure 5. Further NMR spectra of samples **5**, **6** and **8** can be found in Figure S5 in the Supporting Information section. All signals are assigned to the multi-block copolymer structure, which is included within Figure 5. Additional signals – not belonging to the copolymer – can be assigned to the stabilizer of commercial THF, *i.e.*, butylhydroxytoluene (BHT). After the fractionation, the multi-block copolymer samples were enriched with BHT due to the utilized eluent THF in the SEC system. Determination of the block ratio of pS and pTHF requires integration of the corresponding polymer backbone signals and the subsequent calculation of the ratio percentage. For poly(styrene), the resonance associated with $-\text{C}_6\text{H}_5$, m (5H), and for poly(tetrahydrofuran) the $-\text{OCH}_2$ signal, a (4H), were chosen for the integration. At the chemical shift of the pS backbone signal m, the aromatic protons of BHT are detected as well. Thus – initially – the BHT signal part had to be eliminated from calculations, before deducing the pS : pTHF ratio. The calculated ratios of each multi-block copolymer **5-8** are collated in Table 3 and compared to the theoretical values. The theoretical fractions in percentage of pTHF and pS are calculated from the initially employed equivalents (which are based on the pS and the prepolymer chains) and referred to the repeating units of styrene and THF within the polymer. Although the values determined via NMR differ from the

theoretical values due to the fractionation process, it can be observed that an increasing amount of pTHF during the synthesis results also in a higher pTHF content in the copolymer structure. In ideal cases – due to the polyaddition process – the ratio of prepolymer to polystyrene diol should not deviate from an equimolar ratio because of the alternating polymer structure. However, in the polymerization process of polyurethanes it is commonly known that the highly reactive isocyanate groups of the prepolymer can undergo side reactions, e.g., they undergo dimerization or – if traces of water are present in the reaction flask – two isocyanate groups can form an urea bond, liberating carbon dioxide.³² In case of sample **5**, in which a lower pTHF content than 50% is calculated via NMR, it is certain that the copolymer structure possesses polystyrene on both chain termini.

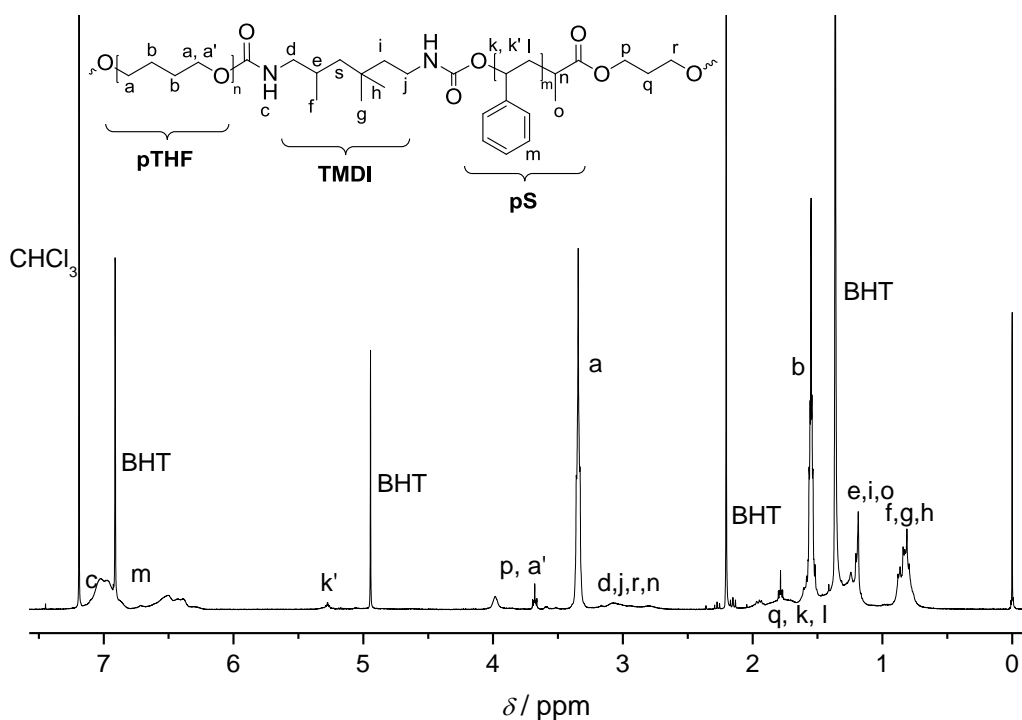


Figure 5 ¹H-NMR spectrum of the multi-block copolymer pS-*b*-pTHF **7** after fractionation. Due to the fact that the SEC eluent used for the fractionation contained

BHT, the inhibitor is visible in the NMR spectrum. However, the BHT content can be quantified and the integral of the resonance m can be corrected.

Table 3 Collation of the results concerning the fractions in molar percentage of the individual blocks in the multi-block copolymer samples obtained via NMR (fraction NMR). The results are compared to the initially employed content based on the repeating units of the homopolymers pS and pTHF in the reaction flask (fraction theo.).

Sample	<i>pS</i> <i>fraction</i> <i>theo.</i> %	<i>pTHF</i> <i>fraction</i> <i>theo.</i> %	<i>pS</i> <i>fraction</i> <i>NMR</i> %	<i>pTHF</i> <i>fraction</i> <i>NMR</i> %
5	74	26	61	39
6	65	35	47	53
7	56	44	48	52
8	48	52	34	66

In addition to NMR spectroscopy, FT-IR ATR measurements of the multi-block copolymers were conducted to confirm the molecular structure of the block copolymers. Figure 6 depicts the infrared absorbance of the multi-block copolymer molecule **8** after fractionation. The very similar IR spectra of the samples **5**, **6** and **7** are shown in Figure S6 of the Supporting Information section. The signal at 1724 cm^{-1} is associated with the -C=O of the urethane moiety linking the pTHF and pS blocks. The IR absorbance at 1110 cm^{-1} correlates with the -CO- stretching vibration of the pTHF backbone while the signals at 1493 cm^{-1} as well as at 700 cm^{-1} and 749 cm^{-1} are associated with the pS polymer structure. Again – as described in the context of the

NMR spectra – BHT is included in the samples, which explains for example the strong absorbance at 700 cm^{-1} due to the overlapping of absorbance intensity resulting from pS and BHT.

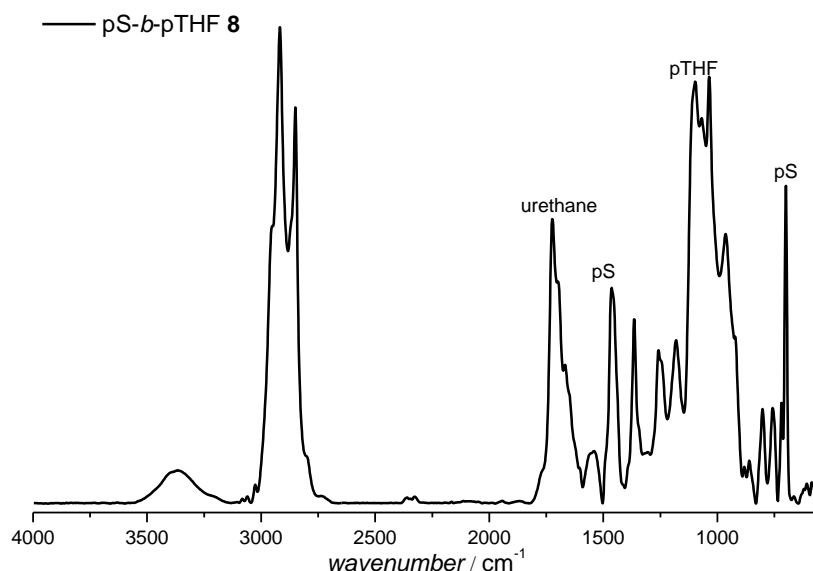


Figure 6 FT-IR spectrum of the multi-block copolymer **8**, after fractionation, determined via ATR. The significant bands and signals derived from the vibrations of the urethane linkage, the pTHF and the pS backbone are labeled within the figure.

Even more details of the multi-block copolymer structure can be obtained by SEC on-line coupled to infrared spectroscopy. With such an on-line SEC-FT-IR system, 12 complete infrared spectra (each 50 scans) per minute are collected with a resolution of 4 cm^{-1} . Because of the low concentrations in SEC, the IR spectra mainly show solvent signals and only small changes during the elution results from polymer signals. To suppress the constant solvent signals a second order polynomial is fitted for every wavenumber to reference data taken before and after the chromatogram – in a region where the RI detector displayed that no polymer was present – to determine exclusively the solvent signals and the drift. This second order polynomial is

subsequently subtracted from the time evolution at this wavenumber. After the baseline correction and smoothing a 2D spectral chromatogram is obtained, from which each chromatogram for each component can be extracted. For a more detailed description of the SEC/FT-IR setup, the reader is referred to reference 25.

In Figure 7, the SEC elugrams of the multi-block copolymers **5** and **8** detected via the absorbance intensity at the specimen wavenumbers 1493 cm^{-1} (aromatic ring of pS) and 1110 cm^{-1} (CO in pTHF), respectively, are illustrated. The SEC/FT-IR elugrams of **6** and **7** can be found in Figure S7 in the Supporting Information section. The wavenumbers were chosen after measuring pTHF and pS homopolymers with the online SEC-IR system. pTHF does not show any absorbance at 1493 cm^{-1} , where the signal of the phenyl ring of the pS polymer is detected, whereas pS does not show any absorbance at 1110 cm^{-1} , at which pTHF shows strong absorbance due to the --CO ether stretching vibration in its polymer backbone. Thus, an ideal situation for the individual integration of each signal is given. The elugrams in Figure 7 show the signal intensities derived from the pS and the pTHF content, respectively, as a function of the elution volume, from which the molar mass can be derived. The elugrams are overlapping very well, which signifies that at all molar masses poly(styrene) and poly(tetrahydrofuran) are incorporated and thus no blend of two homopolymers was produced.

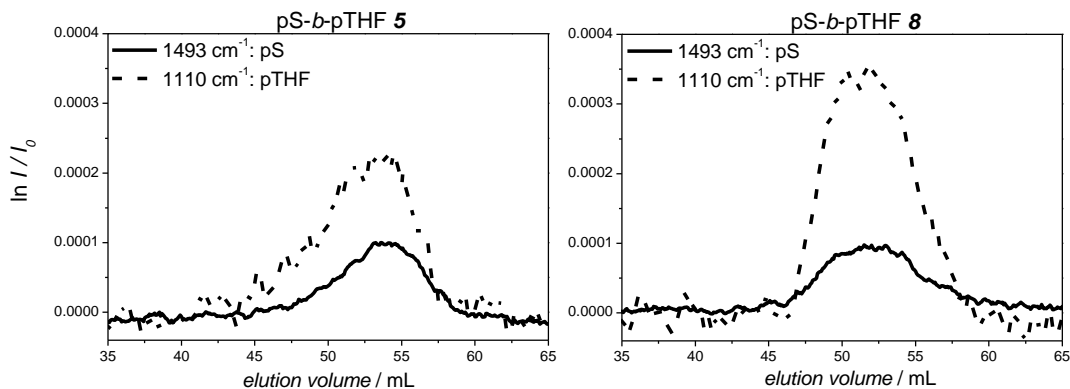


Figure 7 Elugrams of the multi-block copolymer samples **5** and **8** measured via SEC-IR. Two wavenumbers are depicted at 1493 cm^{-1} and 1110 cm^{-1} , which correspond to the vibration of the aromatic ring in poly(styrene) and the CO stretching of the poly(tetrahydrofuran), respectively.

Determining the content of one block in the multi-block copolymer structure at a certain molar mass, however, requires a calibration of the signal intensities. For this purpose pS/pTHF polymer blends with known concentrations were injected into the SEC-IR system and the signal intensity was detected. All information associated with the calibration of the SEC-IR system can be found in the Supporting Information section (see Figure S8). By plotting the signal intensity vs the amount of absorbing units and a subsequent linear regression the slope was calculated. The value of the slope was applied on the absorbing intensities in the SEC-IR elugrams. In Figure 8, the SEC-IR elugrams of the multi-block copolymers **5** and **8** after application of the calibration correction, are depicted. These elugrams correlate with the amounts of pS and pTHF present in the sample. In the lower half of Figure 8 the ratio of the pS and the pTHF content in the multi-block copolymer sample is illustrated as a function of the elution volume. Ratios are only calculated for values larger than 5% of the peak

maximum in the chromatogram, because noise dominates the regions beyond. It can be observed that the two samples exhibit differences in their multi-block copolymer structure. The pS content of sample **5** is increasing from 30% to 70% with increasing elution time, whereas the pS content of sample **8** is not changing during the elution process. Thus, the multi-block copolymer sample **5** possesses a gradient in its constitution, whereas the relative composition in sample **8** is independent of the molecular weight. The elugrams and ratios as a function of the elution volume for sample **6** and **7** are given in Figure S9 in the Supporting Information section. Both samples, **6** and **7**, show only a very slight increase in the pS content as a function of the elution volume. From the initial SEC elugrams it is known that sample **5** has a rather low molecular weight, compared to sample **8**. Furthermore, the pS content in sample **5** was chosen much higher than the pS content in sample **8** during the synthetic process. Consequently, the chain ends of sample **5** are very likely pS terminated. While for an ABA triblock copolymer the ratio of pS to the prepolymer is 2:1, it shifts to a 3:2 ratio for an ABABA pentablock copolymer. Following this reasoning, the ratio becomes closer to one for higher molar masses. As a result, the pS content in sample **5** increases with increasing elution volume. In other words, at lower molecular weights (i.e. higher elution volumes) the influence of the chain termini (in this case pS) on the overall composition becomes more and more influential, thus increasing the fraction of pS towards higher elution volumes.

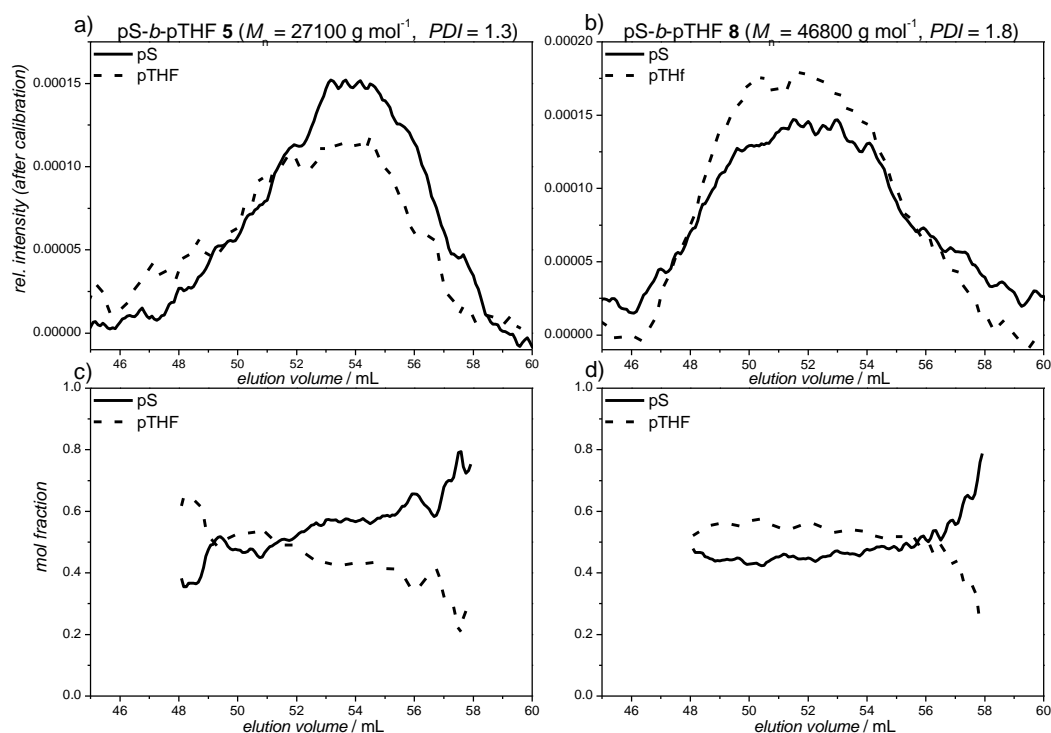


Figure 8 a) and b) Calibrated online SEC-IR measurements of the multi-block copolymer samples **5** and **8**. Figure 8 c) and d) show the block poly(styrene) and the poly(tetrahydrofuran) fractions, respectively, in the multi-block copolymer as a function of the elution volume of the SEC system and thus on the molar masses of the multi-block copolymer samples.

By integrating the calibrated elugrams, the overall amount of pS and pTHF present in the multi-block copolymer sample can be calculated. Ideally, if the sensitivity of this newly developed SEC/FT-IR method is sufficiently high, the values should be in-line with the ratios obtained via NMR. In Table 4, a summary of the data obtained via the different analytical methods is provided. Figure 9 visualizes the same data in a graph. The amount of pTHF (in mol-percent) obtained via NMR integration and SEC-IR measurements, is directly compared. The pTHF content calculated on the basis of the NMR spectra correlates very well with the one obtained via integration of

the calibrated SEC-IR elugram. The molar masses obtained from conventional SEC and triple detection differ as a result of the different detection methods and of the fractionation process that was performed before the analysis with triple SEC. However, the fractionation process was necessary to obtain absolute molecular weights of the pure multi-block copolymers.

A possible explanation for the observed increase in average molar mass of the multi-block copolymers with increasing amounts of pTHF, is the formation of an urea bond additionally to the urethane bond, which occurs in the presence of water residues with two isocyanate groups. Via such an additional reaction, more pTHF can be incorporated into the multi-block copolymer and – thus – the molar masses increase, too.

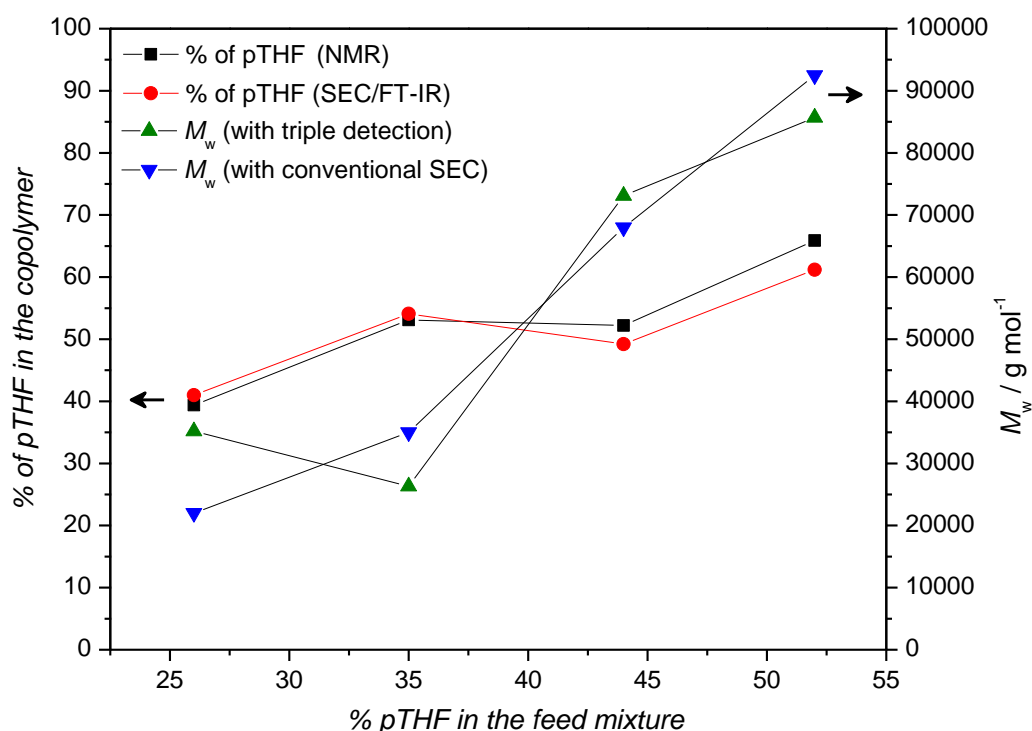


Figure 9 Correlation between pTHF mol fraction in percentage in the feed mixture and the pTHF content in the resulting multi-block copolymers **5-8** obtained via two

analytical methods, *i.e.*, online SEC-FT-IR and ^1H -NMR. In addition, the obtained weight-average molar masses as a function of the initial pTHF fraction are depicted.

Table 4 Collated data of the molecular specifications of the synthesized multi-block copolymers.

Sample	Eq prepolymer:pS	$M_w / \text{g mol}^{-1}$ (LS)	$M_w / \text{g mol}^{-1}$ (RI)	<i>pTHF</i> fraction <i>theo.</i> %	<i>pTHF</i> fraction NMR %	<i>pTHF</i> fraction IR %
5	1:1.5	35200	22000	26	39	41
6	1:1	26300	35000	35	53	54
7	1.5:1	73100	68000	44	52	49
8	2:1	85700	92500	52	66	61

Conclusions

In the current contribution a procedure of switching the RAFT end group of a polymer chain to a hydroxyl function was successfully employed to synthesize diol terminated poly(styrene). The macro-diol was subsequently reacted with a diisocyanate end-functional poly(tetrahydrofuran) to obtain high molar mass multi-block polyurethanes. The multi-block copolymer structure and its size were determined by a variety of analytical methods such as SEC with triple detection, LACCC, NMR and SEC coupled on-line to FT-IR. It was demonstrated that the NMR and on-line SEC-FT-IR measurements show highly comparable results for the quantification of the exact composition of each polymer structure, evidencing the power and the sensitivity of the newly introduced on-line SEC/FT-IR coupling

technique for elucidating polymer structures. The current contribution has thus evidenced that high molecular weight polyurethanes ($M_n = 46800 \text{ g mol}^{-1}$, $M_w = 85700 \text{ g mol}^{-1}$) based on polymer chains made by RAFT can be accessed in a reproducible fashion. The presented general synthetic approach can be readily applied to other ω -functional hydroxyl polymers that are accessible via the RAFT processes and the thiocarbonyl thio to hydroxyl switch protocol.

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Supporting Information Available. SEC elugrams of the prepolymer **4** and the multi-block copolymers **5-7**, the SEC trace of the repeated synthesis **9**, the $^1\text{H-NMR}$

spectra of samples **5**, **6** and **8**, the IR spectra of sample **5-7**, SEC-IR elugrams of sample **6** and **7**, calibration data for SEC-IR and calibrated elugrams as well as block fractions of the samples **6** and **7** are included in the Supporting Information section. This information is available free of charge from the internet at <http://www.acs.pubs.org>

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TOC Graphic

Multi-Block Polyurethanes via RAFT End-group Switching and their Characterization by Advanced Hyphenated Techniques

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Wilhelm, Filip E. Du Prez and Christopher Barner-Kowollik*

