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Benchtop NMR Coupling to Liquid Chromatography

Chemically-selective detection in Size Exclusion Chromatography

A growing application for benchtop NMR spectrometers is their coupling to existing liquid chromatography methods, such as size exclusion chromatography (SEC) for polymer separations. Polymer chemists can obtain molar mass distributions, perform selective monitoring of functional groups in co-eluting polymer blends and block copolymers, and in favorable cases resolve geometric and positional isomers during separation. SEC is a well-established method used in academic and industrial labs for chemical analysis, preparative scale fractionations, as well as quality control.

In this application note, we describe how benchtop NMR can be coupled to SEC for use as a chemically selective detector. Here, 1D spectra are acquired during continuous flow of the mobile phase through the spectrometer.

Background

High-field superconducting spectrometers were first used for high-performance liquid chromatography (HPLC) eluate detection nearly 40 years ago and such HPLC-NMR hyphenation methods are now common in several industrial sectors, especially when combined with mass spectrometry. Although the method will continue to develop towards using higher fields, a different evolution has occurred in the method for benchtop NMR spectrometers, whose advantages include lower running cost, ease of use, and smaller footprint. An ongoing research effort to develop coupled methods towards better sensitivity is described in a series of published journal articles and Ph.D. theses [1-13], which have a focus on the analysis of polymers by benchtop SEC-NMR and recently small molecules by LAC-NMR using reverse-phase separations. The setup for benchtop LAC-NMR is nearly identical to that used for benchtop SEC-NMR. This separation mode and its applications are discussed in a follow-up article. The Link will be available here, when we upload the next appnote on this topic!

In an SEC separation, homopolymers are separated by their entropic exclusion from a pore network with sizes matching the molecular solvated ‘size’ (**Figure 1**). The pores (~10-100 nm diameter) are produced by a special polymerization process that incorporates the network structure inside and on the surface of spherical gel particles (~5 μm), which are packed into separation columns under high pressure to produce a stable stationary phase with high surface area. Separation columns are nowadays purchased as off-the-shelf components. The chemical structure of the stationary phase is usually chosen to minimize interactions with the polymer and mobile phase, as only the exclusion mechanism is desired; polystyrene crosslinked with divinyl benzene is a common option. Mobile phase is pumped through the column under high pressure and the dissolved polymer is injected as a plug at the head of the column. The polymer’s solvated size determines the extent to which they can enter the pore network, and this exclusion mechanism determines the elution order. The smallest chains, for example, are able to permeate a large proportion of the pore network, whereas the largest chains are sterically excluded from most of the pores. Chains then elute in order of decreasing molar mass, as shown by an external calibration of the separation column.

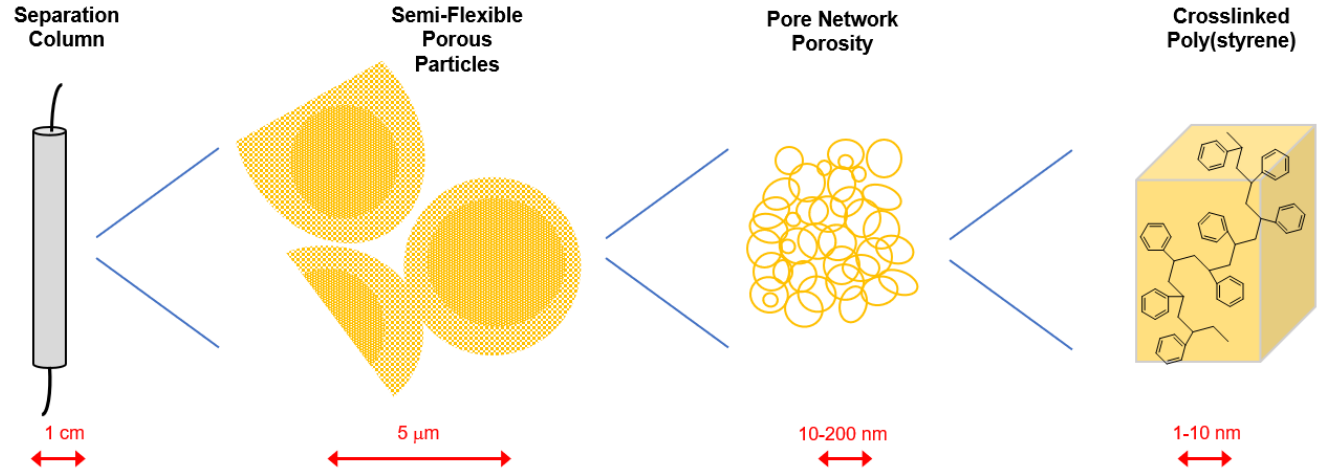

Figure 1. Lengths scales involved in SEC separation: column (1 cm), stationary phase particles (5 µm), porous network (10-200 nm), and chemical structure (0.1-10 nm).

A conventional SEC analysis of polystyrene homopolymers is typically carried out with a mass-sensitive detector, e.g. differential refractive index (DRI). A distributional analysis follows based an external calibration of the separation column (**Figure 2**), typically with the functional form $\log_{10} M = A + Bt_{el}^{1} + Ct_{el}^{2} + Dt_{el}^{3}$, from which calibrated molar mass averages can be determined (here, t_{el} is the elution time, and M refers either to the mass-average molar mass M_w or to the 'peak' molar mass provided by manufacturer of the reference polymer). Some example analyses of polystyrene with differing distributional width are illustrated to show the basic capability of this method. Here, Đ is the dispersity defined as the ratio M_w/M_n, where M_n is the number-average molar mass: **A**. Calibration reference: M_w = 956 kg/mol, Đ = 1.4. **B**. Broad dispersity reference: M_w = 246 kg/mol, Đ = 2.9; **C**. Light-scattering reference: M_w = 87.6 g/mol, Đ = 1.1; **D**. Commodity product (coffee cup lid): M_w = 210 kg/mol, Đ = 21.

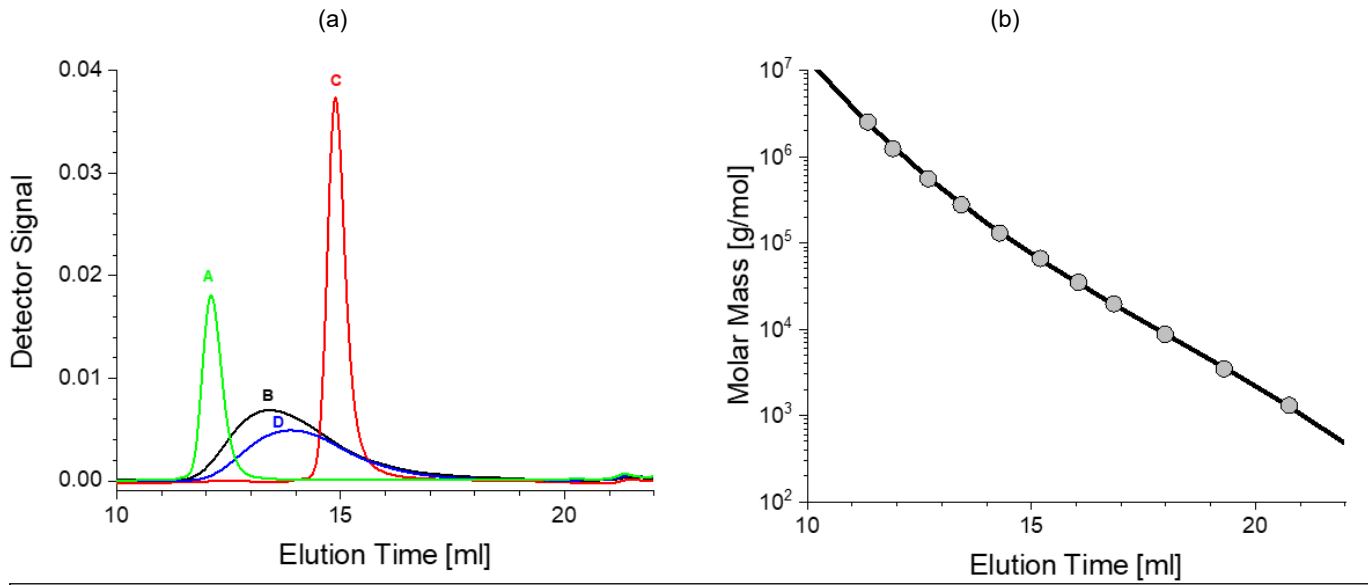

Figure 2. Conventional SEC analysis of example polystyrene (PS) homopolymers, which have been separated in THF and detected with a mass-proportional detector. (a) chromatograms; (b) external column calibration.

However, contemporary SEC development usually centers on the challenges of more complex samples or mixtures, which may contain hetero- and homopolymers of many types with overlapping distributions of molar mass, branching and/or topology, functionality, sequence distribution, chain stiffness, etc. Such complex mixtures or blends are necessary in many practical applications, for improving melt processability, fine-tuning of properties, altering interfacial tension, or other more complex reasons. Such mixtures are

challenging for SEC detection for 2 reasons. First, the SEC has low resolving power as a separation process, and even high-resolution columns and setups are not able to separate polymers fully by their chain length, except for certain oligomers. When polymers of different chain length elute at the same time, or co-elute, the signal output is a sum over all components within the detection cell. Secondly, detectors that are common in polymer analysis, such as the differential refractive index (DRI), ultra-violet (UV), viscometer (VISC), and light-scattering (MALS) detectors, are not chemically-selective, but rather respond in proportion to segment concentration c and a molar mass factor (e.g., DRI~c, UV~$c_{chromophore}$, MALS~cM^1, VISC~cM^{α} where α=0.5-0.8 for random coils). Sorting out the various eluting components usually requires a multi-detection setup, designed so that one detector is able to respond *selectively* to one polymeric component (or component of the distribution) and the other detector can respond selectively the second component.

^{1}H-NMR spectroscopy, on the other hand, is by definition a chemically-selective detector. Protons of a given organic functional group are identified by their chemical shift δ, spectral splitting pattern (whether singlet, doublet, multiplet, etc, as a result of spin-spin coupling), and relative proton abundance. Under quantitative acquisition conditions, the instrument is an absolute proton detector, and relative proton abundance in different functional groups can be determined readily. Although there are challenges to acquire under true quantitative conditions in continuous flow NMR, in many cases a semi-quantitative acquisition is sufficiently accurate for many analysis goals. This unique ability to distinguish different organic functional groups in the same detector cell, and estimate their concentration simultaneously in a continuously flowing eluent, lies at the heart of the coupling of benchtop NMR to SEC separations.

Experimental Setup

To set up an existing HPLC system for benchtop SEC-NMR, the spectrometer is added as the first detector, followed by additional detectors, with DRI placed for safety last in the series. A current setup is shown in **Figure 3**, which uses a quaternary HPLC pump, manual rotary injector, a thermostatted column compartment, and the following detectors in series: (i) spectrometer (80 MHz, proton optimized); (ii) ultraviolet (UV); (iii) differential refractive index (DRI). Flexible PTFE capillaries are used to pass eluate from the column oven to the NMR flow cell, and from the flow cell back to the UV detector. The glass flow cell has a cylindrical profile at the detection volume and an entrance cone to eliminate turbulent mixing at a mobile phase flow rate of 1-2 ml/min. PVDF fittings for the flow cell are available in Magritek's flow kit. The capillary lines from the column to the flow cell are insulated using flexible foam. Further details are found in **Table 1**.

(a) (b)

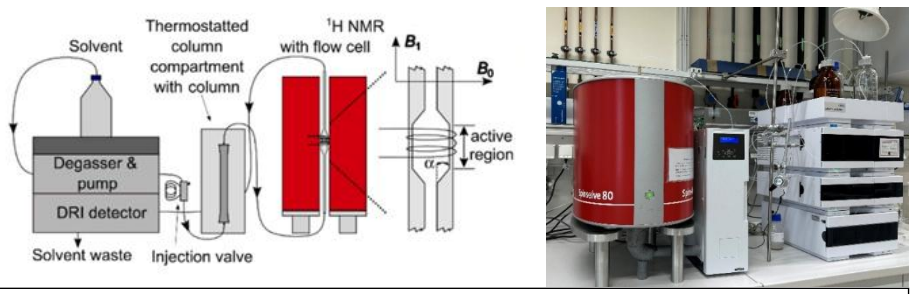

Figure 3. (a) Schematic of benchtop SEC-NMR components [9]; (b) photograph of system in use.

Component	Description	Notes
Solvent Reservoir	THF, $CHCl_3$, H_2O, Acetone, Methanol, etc.	Use HPLC-grade, freshly opened solvents. Check for influence of added compounds on spectral interference (e.g., antioxidants BHT and amylene, H_2O)
Pump	Quaternary Pump (Agilent 1260 Infinity II)	
Degasser	Integrated (internal volume 1.5 ml)	
Injector	Manual: Rotary with magnet trigger, Rheodyne 7725i. Auto: Agilent 1260	Manual: Stainless steel injection loops: 10 µL, 100 µL, 500 µL, 1000 µL. Higher-than-standard loadings required, typically 500 µL is used. Auto: 500-900 µL injection volume

Column	SEC: 25 x 300 mm. Stationary Phase: (i) Styrene-Divinyl Benzene (PSS Agilent) LAC: 10 x 250 mm. Stationary Phase: (i) C-18 bonded silica (Machery-Nagel)	Larger diameter columns (often designated semi-preparatory) are needed to ensure accurate peak shape at flow cell and boost sensitivity.
Thermostatted Column Compartment	PSS/Extrema TCC 6500 for Agilent 1260	Column(s) must be thermostatted at 26.5 °C, to match the magnet temperature. (Variable temperature options are available) Use side entrance/exit ports for minimizing capillary length.
^{1}H-NMR Spectrometer	80 MHz, proton-optimized probe	Spectrometers with other configurations are available and have been tested.
UV Detector	Agilent 1260 VWD (G7114A)	
DRI Detector	Agilent 1260 RID (G1362A)	
Capillaries	Flexible PTFE (ID=0.25 mm)	Preferably <1 m in length.
Flow Cell	Glass, with cylindrical shape over sensitive volume (ca. 200 μL), with entrance and exit cone; total volume ca. 1000 μL; measurement volume ca. 60 μL. [4,10] Fittings: Magritek Flow kit.	
Insulation	Expanded PP	Insulation of capillary between oven and flow cell is necessary for stability. Test for insulation effectiveness using temperature/field monitor.
Software	WinGPC (PSS Agilent) Spinsolve Expert (Magritek)	

Table 1. Hardware used for setup of benchtop SEC-NMR and LAC-NMR.

Polymer Blends (Mixtures)

Two examples below illustrate how to use the coupled benchtop spectrometer for selective detection of polymer functional groups in mixtures separated by SEC. In the first example (**Figure 4**), a 50/50 blend of polyethylene oxide (EO) (M=4 kg/mol) and polypropylene oxide (PO) (M=2 kg/mol) are separated in chloroform. These two polymers were chosen to illustrate the method for fully separated polymers. The time-resolved spectra are visualized using a waterfall plot. Here, 12 scans were averaged to produce 1 spectrum, resulting in a 20 sec interval between time slices (labelled elution increment). The first polymer to elute is the EO (peak **a**), and the second is the PO (peak **b**). For clarity, the spectral slices at the peak maxima are overlaid at the top of the graph, where we are able to identify the two polymers based on aliphatic protons. The PO can be uniquely identified by the partially resolved methyl doublet (**3**, δ 1.16 and 1.11 ppm), whose signal is free and clear of interference from either other EO protons or water contaminant. The methylene resonance of EO (**4**, δ 3.65 ppm) is only partially resolved from the methylene of PO (**1**, δ ≈3.57 ppm), and both signals also overlap to some extent with the PO methine signal (**2**, δ 3.47 ppm). Thus, these signals are not the best option for detecting PO. A chromatogram, also called an elugram, is obtained by plotting the intensity of the NMR signals as a function of the elution time. In this example, the line intensity, i.e. peak height, is plotted, rather than the numerical integral, which allows a quick analysis and a low-risk, qualitative judgement on the presence (or absence) of a particular functional group across the chromatogram. The PO polymer can be clearly identified using its methyl group doublet, corresponding indeed to peak **b**, whereas the remaining signals appear on both peaks **a** and **b** in the chromatogram owing, again, to signal overlap. We thus see here the importance of method development in identifying signals selective to only of the polymers in a mixture. A comparison of static ^{1}H spectra of each mixture component, in the search for uniquely identifying signals, is indeed usually the first step in preparing for an SEC-NMR experiment.

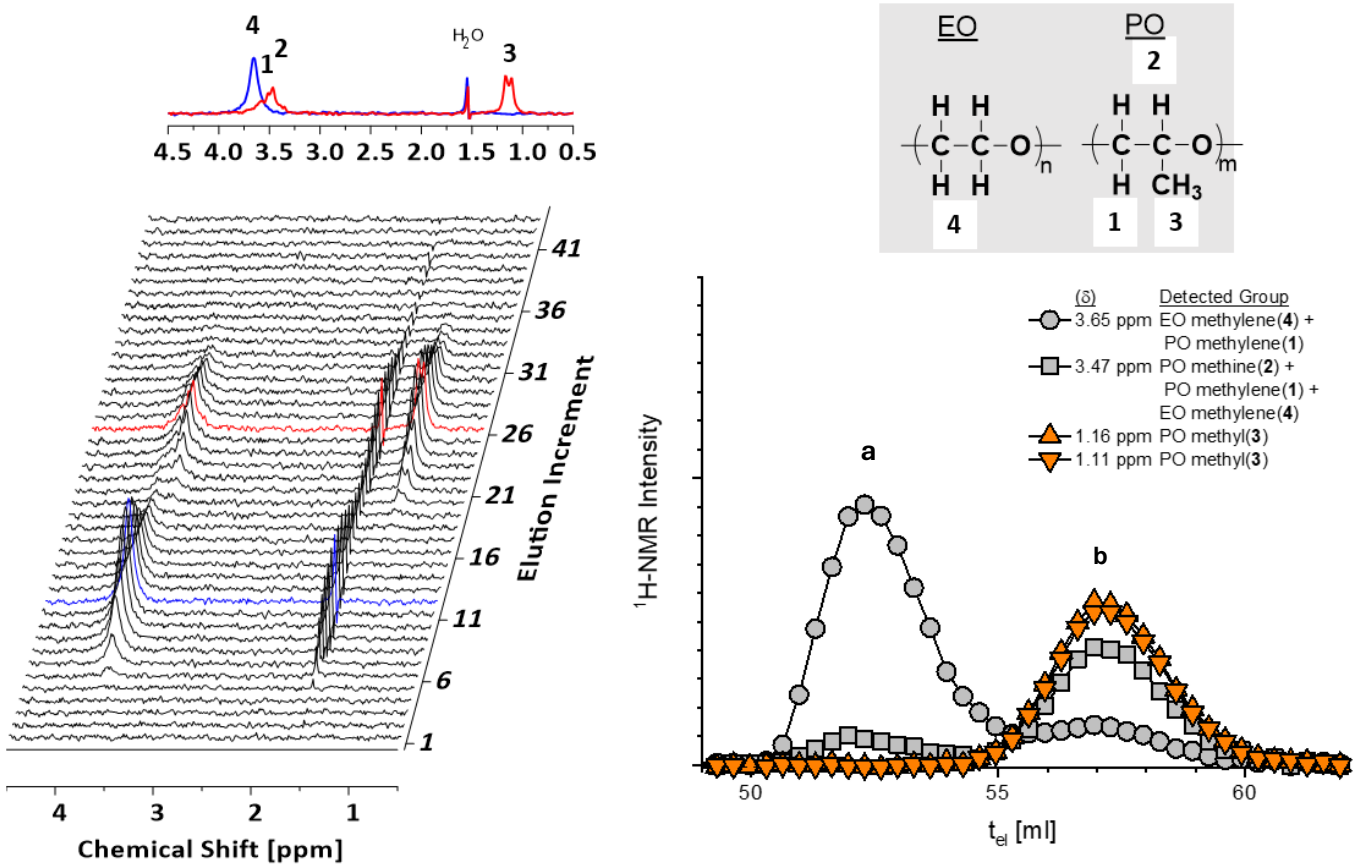

Figure 4. Benchtop SEC-NMR of a blend of polyethylene oxide (EO) with molar mass of 4 kg/mol and polypropylene oxide (PO) with molar mass 2 kg/mol. The detection of PO is monitored independently using the methyl doublet (**3**, δ 1.16 and 1.11 ppm), whereas the methylene resonance (**1** δ 3.65 ppm), and the methine resonance (**2**, δ 3.47 ppm) are common to both EO and PO.

In the second example (**Figure 5**), a blend of polystyrene (PS) (M=54 kg/mol) and polymethyl methacrylate (M=23 kg/mol) are separated in THF. A contour plot illustrates the spectral intensity as a function of two variables: the chemical shift δ along the x-axis, and the elution volume V_{el} along the y-axis from top to bottom. Here, only 4 scans were averaged to produce 1 spectrum, giving a time interval between spectra of only 2 sec, for increased time resolution. The first polymer to elute is PS (red line) and the second is PMMA (blue line). The spectral slices at the peak maxima are shown at top, where all the protons are labelled and assigned to their respective molecular structure. Some protons appear less suitable for monitoring owing to solvent interference, but we do find one proton signal that uniquely identifies each polymer: PS protons *ortho* to the backbone (**3**, δ 6.54 ppm) and the PMMA methyl singlet (**8**, δ 3.59 ppm). The elugram at right plots the NMR intensity at specific chemical shift values δ in combination with the trace of the DRI detector. Here we see clearly the advantage of using NMR to selectively detect the PS and PMMA polymers individually, because the DRI detector is non-specific: its signal is a summed response from both polymers.[4]

In these two examples of polymer blend separation, a second inline detector is not needed for monitoring the 2nd polymeric component, as the benchtop NMR is itself chemically-selective: (i) for the EO/PO mixture, the PO is selectively detected at its methyl group and both polymers are monitored using the combined methylene and methine signal; (ii) for the PS/PMMA mixture, the PS and PMMA are both selectively detected, at the phenyl ring *ortho* protons and methoxy methyl protons.

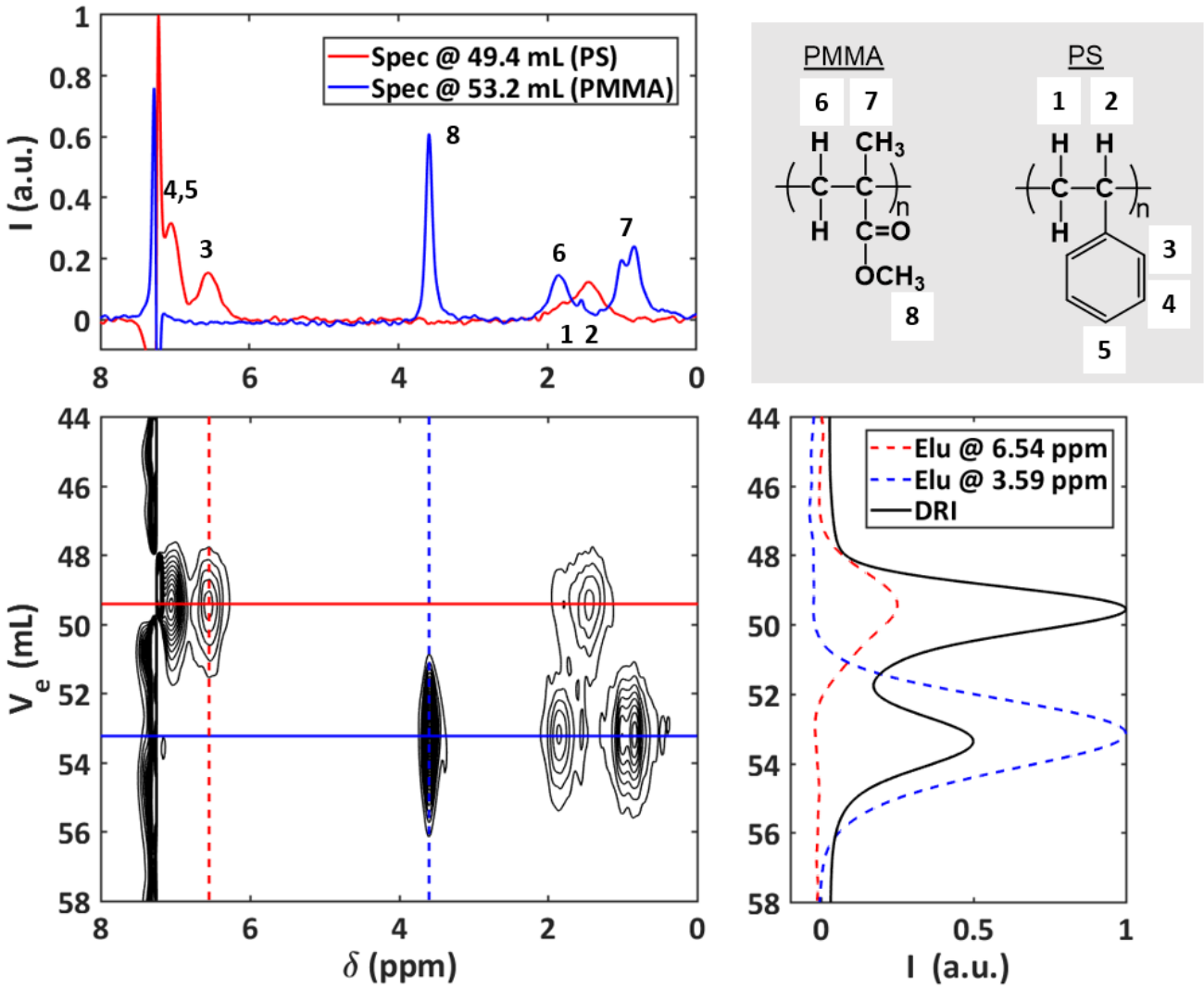

Figure 5. Benchtop SEC-NMR analysis of a 1:1 blend of polystyrene (M_w = 54 kg/mol)) and polymethyl methacrylate (M_w = 23 kg/mol) shown as a contour plot with spectral slices at fixed elution time (top) and line elugrams at fixed chemical shift δ (right). The two peaks can be identified individually due to selective detection: PS protons *ortho* to the backbone (**3**, δ 6.54 ppm) and the PMMA methoxy methyl singlet (**8**, δ 3.59 ppm).[4]

Block Copolymers

Linear block copolymers, synthesized by covalently linking two pure homopolymers together, often show compositional drift or the presence of contaminants (e.g. chains terminated early during synthesis, dimers formed by termination reaction). Two examples below illustrate an evaluation of the composition of block copolymers across their molar mass distribution, and additionally give hints on how low molar mass impurities might be analyzed by benchtop SEC-NMR. In the first example (**Figure 6**), a diblock copolymer of polydimethylsiloxane (PDMS) (M = 14 kg/mol) and polyisobutene (PIB) (M = 3.5 kg/mol) has been evaluated by benchtop SEC-NMR. Here, 12 scans were averaged to produce 1 spectrum, giving a 16 sec time interval between consecutive spectra in the waterfall plot. When this diblock copolymer is separated in chloroform, two peaks elute rather than one. To facilitate more quantitative analysis, the elugram here was calculated using the numerical integrals across each spectral peak. The PDMS is uniquely identified by the methyl singlet (**1**, δ 0.07 ppm), whereas the PIB is uniquely identified from its methylene resonance (**3**, δ 1.41 ppm), and its methyl resonance (**2**, δ 1.11 ppm). The first peak to elute (peak **a**), therefore, is the expected diblock copolymer. The second peak to elute (peak **b**) lacks a PDMS signal while showing weak PIB signals. A further analysis is possible from the two unique signals: the mol% PIB can be calculated as $100*(I_{PIB}/3) / (I_{PIB}/3 + I_{PDMS}/6)$, where I_{PDMS} is the spectral area of proton **1** and I_{PIB} is the

spectral area of proton **2**. The mol% PIB is then plotted just above the elugram with the same elution volume axis. Here we observe a broad composition variation of ca. 80-20 mol% PIB across the first diblock copolymer after separation, whereas the stated composition of this block copolymer was 75 mol% PDMS. The second peak is verified to be mainly PIB, based on this analysis, and is likely to be leftover contaminant from synthesis. Finally, with a column calibration function at hand, the apparent molar mass of peak **a** is

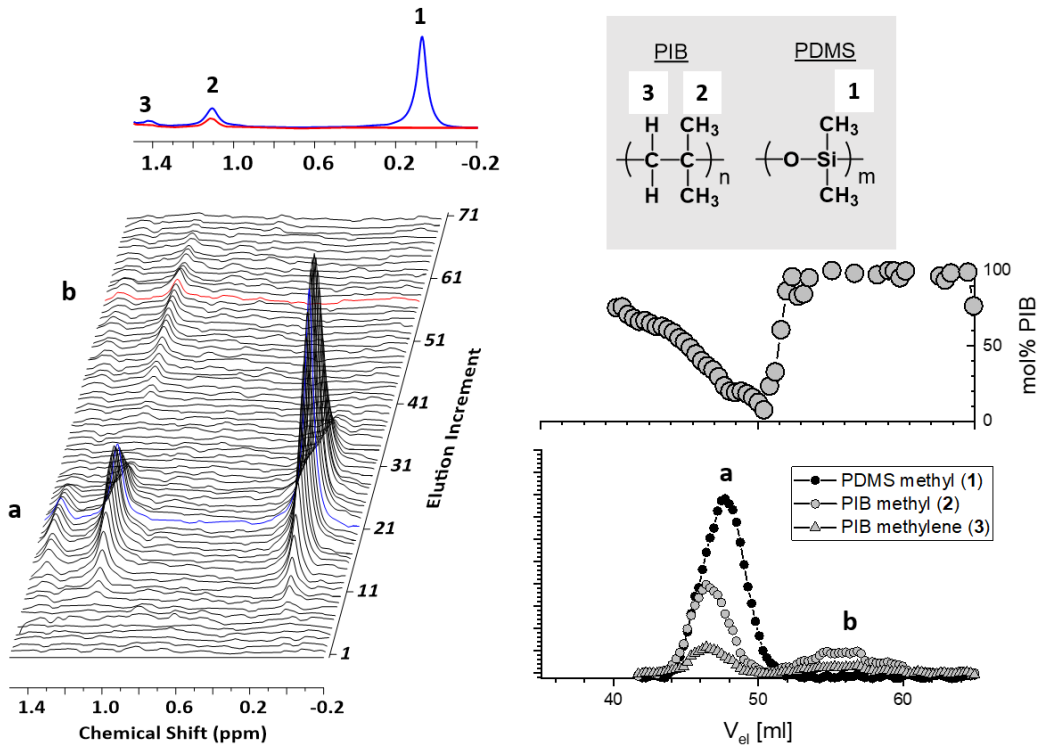

Figure 6. Benchtop SEC-NMR of poly(isobutylene-*block*-dimethylsiloxane). This block copolymer separates into two components, whose composition can be analyzed using signals unique to each block: PDMS methyl (**1**, δ 0.07 ppm); PIB methyl (**2** δ 1.11 ppm); PIB methylene (**3**, δ 1.41 ppm). The majority fraction (peak **a**) consists of block copolymer with composition gradient. The minority fraction (peak **b**), having with lower molar mass, contains no PDMS, as indicated by the absence of signal from proton **1**.

17 kg/mol and peak **b** is 4 kg/mol, which agrees well with the stated specification of 14 kg/mol of the PDMS block and the 3.5 kg/mol of the PIB block.

Besides the identification of low molar mass contaminants in a diblock copolymer, this example is interesting for another reason: PDMS is a classic example of a polymer with difficult detection requirements. It is normally not detectable using DRI or UV detection, as the specific refractive index increment of PDMS is too low and it does not absorb UV. Thus, benchtop NMR detection is an effective solution to this problem.

In the second example (**Figure 7**), a triblock copolymer of ethylene oxide (EO) and propylene oxide (PO) has been evaluated by benchtop SEC-NMR. This triblock copolymer, known by the trade name Pluronic F-127 or Poloxamer 407, consists of a central hydrophobic block of oxypropylene (M = 4 kg/mol), capped on both ends with hydrophilic blocks of oxyethylene (ca. 70 wt% in total). Here, 12 scans were averaged to produce 1 spectrum, giving a 16 sec time interval between consecutive spectra. When separated in chloroform, two peaks elute rather than one. The composition of these two peaks can be analyzed using the selective detection of the methyl doublet of the PO block (**3**, δ 1.15 ppm) and the superposed signals of the backbone methylene of EO and PO (**1**, **4**, δ 3.65 ppm) and the PO methine (**2**, δ 3.47 ppm). Here again we use numerically integrated spectra to create an elugram. The block composition is calculated as follows: wt% EO = $100*33(I_A - I_B) / [33(I_A - I_B) + 58*I_B)$, where I_A is the intensity of the overlapping peaks at δ 3.65 and δ 3.47 ppm, and I_B is the intensity of the methyl peak at δ 1.15 ppm [14]. We find a relatively flat composition profile of ca. 70 wt% in the first peak (peak **a**). The 2nd peak to elute, however, with ca 1.5-2x lower molar mass, contains a much higher percentage of EO, nearing 100% (peak **b**). A number of published manuscripts in fact also provide other evidence that Pluronic-type triblocks can be contaminated by lower molar mass material.[15] We observe no other signals in the spectra except EO and PO. One

interpretation is that the F-127 from this source contains a small proportion of diblock copolymer with EO/PO ratio of ca. 10:1, which could result from premature chain termination during polymerization of the middle PO block.

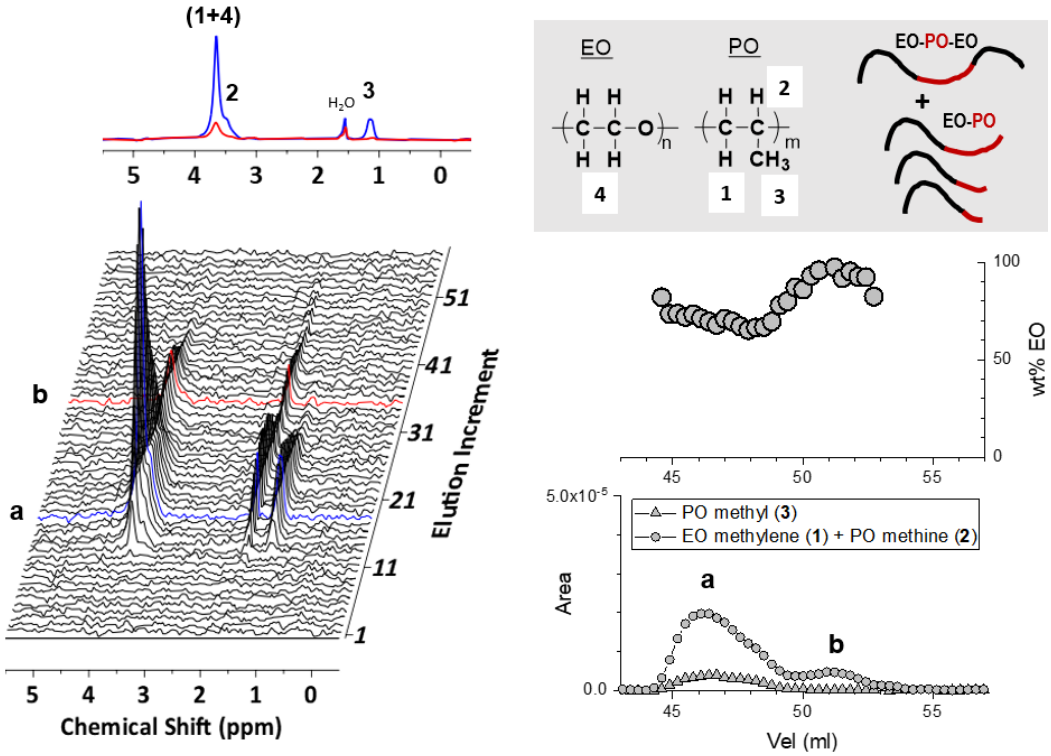

Figure 7. Benchtop SEC-NMR of poly(oxyethylene-*block*-oxypropylene-*block*-oxyethylene) (Pluronic F-127). The two eluting components can be compositionally analyzed using PO's unique methyl group signal (**3**, δ 1.15 ppm) and the combined signals from the PO methine (**2**, δ 3.47 ppm) and methylene groups (**1** & **4**, δ 3.65 ppm). Peak **a** consists of triblock copolymer with ca. 70 wt% EO units. Peak **b** has ca. 90 wt% EO. Thus, NMR indicates the presence of diblock copolymer as a contaminant.

This example is interesting in that further collection and analysis of the contaminant separated out by SEC, by e.g. fraction collection, is not needed; NMR selectivity and the onflow nature of the detection has already given us a very good hint of the unknown component's molecular structure.

Polymers with isomeric repeat units

Polybutadiene (PB), widely used for its tough yet elastomeric properties (e.g. car tires), is a homopolymer synthesized from 1,3-butadiene. This monomer can polymerize by different mechanisms (*cis*-1,4 addition, *trans*-1,4 addition, and 1,2 addition), leading to several isomeric forms with quite different properties. For example, high *cis*-1,4 addition PB has a glass transition, T_g, around -90 to -100 °C and crystallizes readily, whereas high 1,2 addition PB has a T_g around -30 °C and the crystallization depends on presence of syndiotactic segments. The isomeric content is controlled by means of catalysts and processing conditions, leading to PB products with a variety of molar mass, distribution, and isomer ratio. These materials are often further blended into rubber products or chemically grafted (e.g., grafting on polystyrene for high impact materials. The double bond in PB plays a key role in vulcanization reactions, and is also the key to determine isomer ratios.

To illustrate how benchtop SEC-NMR might be used for selective detection of isomers, a mixture study was carried out with two PB isomers, a 1,2-addition PB (M_w = 18.2 kg/mol, Đ=1.02), a high *cis*-1,4 PB (M_w = 18.3 kg/mol, Đ = 1.04). A 50/50 blend of each prepared sample was then analyzed by the same method to show how mixture signals are distinguished (**Figure 8**). The 3 samples were separated in chloroform, and spectra were acquired by averaging 12 scans to produce 1 spectrum, giving a ca. 16 sec time interval between consecutive spectra. The olefinic and aliphatic resonances were assigned to the PB structure using the time slice at the peak maximum. The spectra are shown here as overlays in each case, with numerical integration and chemical assignment indicated for the time slice near the peak maximum. The 1,2-addition PB is uniquely identified by the vinyl protons (**5**, δ 4.98 ppm) and the backbone methylene protons (**3** δ 1.21 ppm). However, the *cis*-1,4 PB does not have a unique identifying resonance, as the

signals from both PBs overlap; in a mixture **1** would overlap with **4**; and **2** would overlap with **6**, respectively. In the 50/50 blend of these two PBs, the elugrams created from signals at δ 4.98 ppm and δ 1.21 ppm show, indeed, the expected mixture signal, whereas the UV elugram (λ=260 nm) is not able to selectively detect these isomers. One presumes here that the weak UV signal is a result of absorption by the double bonds, whose concentration in both PBs is similar. A DRI detector signal, not used in this experiment, would show a similar non-selective response. We see here a very nice contrast between the UV detector, which cannot show a mixture signal, and NMR detector, showing an isomer mixture signal in proportion to molar concentration. A further illustration of this capability is illustrated in the pre-peak material eluting at ca. 40 ml. Though the signal is very weak, NMR is able to pick up absorption at δ 1.21 ppm and δ 4.98 ppm, suggesting that this pre-peak is PB dimer formed by termination of two active PB chains.

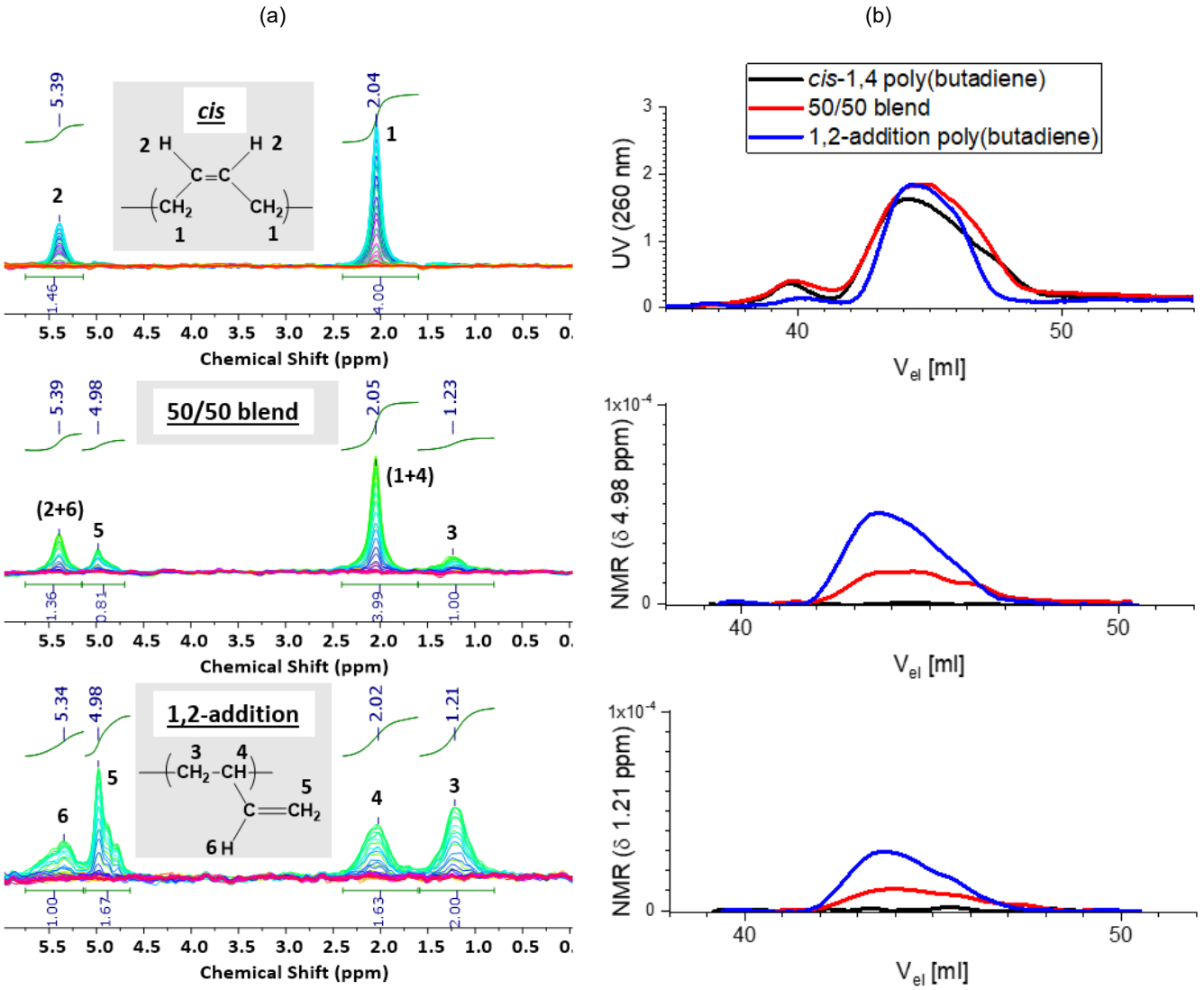

Figure 8. Mixture study of polybutadiene (PB): high-purity *cis*-PB, 1,2-addition-PB, and a 50/50 blend. (a) Spectra acquired during peak elution are stacked together. At the elution maximum, the peaks have been assigned and numerical integrals evaluated. The positional isomer of PB formed by 1,2-addition polymerization is uniquely identified by backbone methylene proton δ 1.21 ppm (**3**), as well as the vinyl proton δ 4.98 ppm (**6**). (b) Elugrams are created from UV-detection (260 nm) and NMR signals at δ 1.21 ppm and δ 4.98 ppm. The UV absorption is non-specific (related to chain unsaturation) and unable to show a mixture signal. However, NMR is able to distinguish the *cis*-1,4 and 1,2-addition isomers in proportion to their molar concentration during elution.

Industrial Polymer Formulations

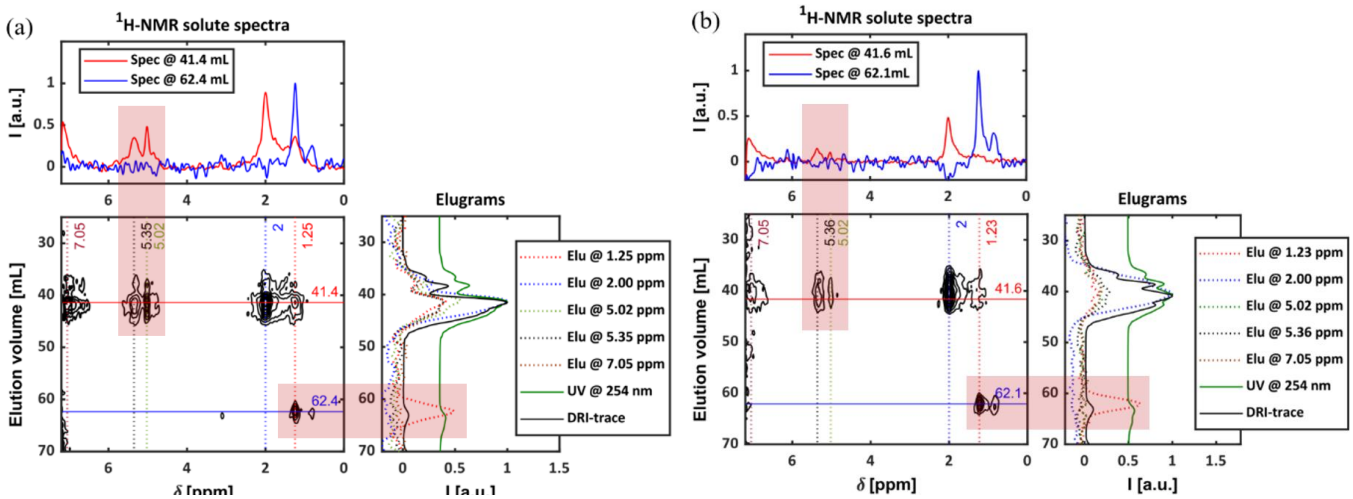

Figure 9. Benchtop SEC-NMR of industrial rubber. These two formulations consist of styrene-*co*-butadiene random copolymers (SBR) having high molar mass and a multimodal distribution. Sample (a) has ca. 24 wt% styrene and a glass transition temperature of -36 °C; sample (b) has ca. 16 wt% styrene and a glass transition temperature of -61 °C. The butadiene content can be monitored using the signals at δ 5.02 and δ 1.25 ppm, and the styrene at δ 7.05 ppm. A low molar mass compound, eluting at 62 mL, can be identified as a hydrocarbon, as only aliphatic protons are observed.[7]

Industrial polymer formulations can also benefit from analysis by benchtop SEC-NMR methods through the detection of formulation contaminants. An example is shown in **Figure 9** using the contour plot visualization, where an industrial rubber formulation has been analyzed to determine the styrene content. An interesting finding was the presence of low molar mass contaminants. Although these components were also detected by DRI and UV, the NMR spectra clearly point to aliphatic protons. This limits the possible contaminants to hydrocarbon oils; stearic acid is used as a lubricant in some rubber formulations and its structure is indeed consistent with the observation.[7]

Conclusion

Overall, the coupling of SEC to benchtop NMR provides a rich set of spectral information for polymer chemists and analysts to obtain better chemical selectivity of polymer-based eluates. Multiple examples have been given in this application note, illustrating how time-resolved 1D spectra can be used to gain chemically-specific information. These examples include (i) the selective detection of a polypropylene oxide in a mixture with polyethylene oxide; (ii) selective detection of both polystyrene and polymethyl methacrylate in their mixtures; (iii) evaluation of block composition of diblock copolymer (poly(isobutylene-*block*-dimethylsiloxane) and triblock copolymer (poly(oxyethylene-block-propylene-*block*-ethylene)) across the molar mass distribution and structural identification of low molar mass contaminants; (iv) selective detection of polybutadiene structural isomers; (vi) analysis of industrial rubber formulations based on random copolymers of styrene and butadiene.

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References

1. Cudaj, M; Guthausen, G.; Hofe, T.; Wilhelm, M. *Macromol. Chem. Phys.* **2012**, *213*, 1933-1943. https://doi.org/10.1002/macp.201200290

2. Höpfner, J.; Ratzsch, K. F.; Botha, C.; Wilhelm, M. *Macromol. Rapid Comm.* **2018**, *39*, 1700766. https://doi.org/10.1002/marc.201700766

3. Botha, C.; Höpfner, J.; Mayerhöfer, B.; Wilhelm, M. 13th Fall Rubber Colloquium **2018**, *118*. ISBN 9783981407631.

4. Botha, C.; Höpfner, J.; Mayerhöfer, J.; Wilhelm, M. *Polym. Chem.* **2019**, *10*, 2230–2246. https://doi.org/10.1039/C9PY00140A

5. Höpfner, J.; Mayerhöfer, B.; Botha, C.; Bouillaud, D.; Farjon, J.; Giraudeau, P.; Wilhelm, P. *J. Magn. Reson.* **2021**, *323*, 106889. https://doi.org/10.1016/j.jmr.2020.106889

6. Georgantopoulos, C. K.; Esfahani, M. K.; Botha, C.; Pollard, M. A.; Naue, I. F. C.; Causa, A.; Kádár, R.; Wilhelm, M. *Phys. Fluids* B **2021**, *33*, 93108. https://doi.org/10.1063/5.0061334

7. Georgantopoulos, C. K.; Esfahani, M. K.; Botha, C.; Naue, I. F. C.; Dingenouts, N.; Causa, A.; Kádár, R.; Wilhelm, M. *Macromol. Mater. Eng.* **2021**, *306*, 2000801. https://doi.org/10.1002/mame.202000801

8. Botha, C.; Matz, M.; Wilhelm, M. Wiley Analytical Science Magazine **2022**. https://analyticalscience.wiley.com/content/magazine-do/wiley-analytical-science-magazine---september-special-issue-2022

9. Matz, M.; Pollard, M.; Gaborieau, M.; Tratz, J.; Botha, C.; Wilhelm, M. *J. Phys. Chem. B* **2024**, *128* (39), 9512–9524. https://doi.org/10.1021/acs.jpcb.4c03509

10. Gaborieau, M.; Matz, M.; Tratz, J.; Pollard, M.; Wilhelm, M. *Macromol. Rapid Commun.* **2025**, *46*, 2500239. https://doi.org/10.1002/marc.202500239

11. Cudaj, M. Medium Resolution-NMR zur chemisch sensitiven Detektion in der polymeren GPC-Analytik. Ph.D. Dissertation, Karlsruher Institut für Technologie (KIT), 2012. https://publikationen.bibliothek.kit.edu/1000025630

12. Botha, C. Method Development of New Chemically Sensitive Detectors for Size Exclusion Chromatography, Ph.D. Dissertation, Karlsruher Institut für Technologie (KIT), 2021. https://doi.org/10.5445/IR/1000130418

13. Matz, M. Entwicklung und Optimierung von Methoden zur Sensitivitätssteigerung in der HPLC-benchtop NMR Kopplung. Ph.D. Dissertation, Karlsruher Institut für Technologie (KIT), 2024. https://doi.org/ 10.5445/IR/1000176793

14. Magritek white paper, „Determining weight percent oxyethylene in poloxamers". https://magritek.com/wp-content/uploads/1915/06/App-note-Pluronic-F127.pdf

15. Batsberg, W.; Ndoni, S.; Trandum, C. *Macromolecules*, **2004**, *37*, 2965-2971. https://doi.org/10.1021/ma030567a

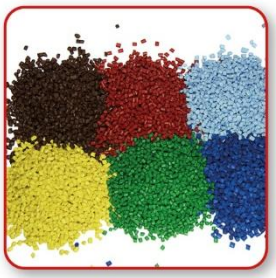
Applications of benchtop NMR spectroscopy

Fine Chemicals

- Structure confirmation
- QC of raw materials without chromatography
- Assay determination
- Impurity profiling

Pharma

- Structural analysis of APIs
- Process monitoring
- Counterfeit detection
- Formulation characterisation
- Excipients quantification
- Assay determination



Polymers

- Molecular weight
- Residual monomer quantification
- Copolymer ratio
- Polymerization monitoring
- Additives

Agrochemicals

- Identity confirmation (fingerprinting vs reference)
- Purity determination (qNMR)
- Residual solvent analysis
- Degradation / stability studies
- Batch-to-batch consistency

Mining

- Quantify ^{7}Li in brines (faster than ICP)
- Real time monitoring of ^{7}Li and ^{23}Na using flow NMR during extraction
- Brine analysis

Batteries

- Solvent composition
- Additive quantification
- Electrolyte degradation
- Residual water analysis
- Ion conductivity and transference

Education

- Hands on experience
- Extensive pulse sequences library
- Multi-nuclear experiments
- Easy to include in practical labs
- Quick reaction analysis

Food

- Quantification of sugars, fat, acids, caffeine, amino acids, alcohol
- Adulteration and origin
- Blend composition
- Fermentation monitoring

Petrochemical

- Total hydrogen content
- Aliphatic to aromatic ratio
- Identifying hydrocarbon types (paraffin, naphthene, aromatics)
- Fuel additives
- Pyrolysis bio-oils

Forensic

- Identification of counterfeit substances
- Structure elucidation of NPS
- Fast identity check
- Purity assessment

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