
THE COUPLING OF LIQUID CHROMATOGRAPHY AT CRITICAL CONDITIONS AND NMR. A NEW TOOL FOR THE CHARACTERIZATION OF POLYMERS

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HPLC-NMR is a very powerful tool for the structure elucidation of complex mixtures. However, it is rarely used for polymers. Most papers are related to GPC-NMR. In these cases slow flow rates as well as deuterated solvents are often used.

The lecture will focus on new applications of HPLC-NMR of polymers. In particular, liquid chromatography at the critical point of adsorption will be used to separate different homopolymers and block copolymers. This method is also called liquid chromatography at critical conditions (LCCC). In case of homopolymers, critical conditions are characterised by a status where the different molar masses elute at the same retention volume. As the consequence, LCCC will separate the polymers according to their chemical heterogeneity. The power of LCCC-NMR was demonstrated at polyethylene oxides for the analysis of different end groups¹. In this case the structure and the length of the end groups could be determined (functionality type distribution (FTD)). Polyethylene oxides were also used to demonstrate the online coupling of 2D-chromatography and NMR. This method combines the separation of the different end groups as well as the molar mass distribution of the polymers.

The main attention of the lecture will be paid to the characterization of copolymers and the microstructure of polymers by coupling of LCCC and NMR.

We have recently shown that LCCC-NMR is the best tool to provide the **true chemical composition distribution and the true molar mass distribution of block copolymers**. Using critical conditions of one block, this block will be considered as chromatographically invisible. The other block, however, can elute in size exclusion chromatography (SEC) mode under certain circumstances. These conditions allow the separation of existing homopolymer from the copolymer. Therefore, it is possible to determine the true chemical composition as well as the true molar mass of the entire copolymer. PS-*b*-PMMA block copolymers of different block lengths were analyzed with LCCC-NMR by using solvent mixtures for establishing critical conditions of poly(methyl methacrylate) (PMMA) and polystyrene (PS)^{2,3}.

The most challenging separation of block copolymers was the development of LCCC methods for analyzing PI-*b*-PMMA copolymers by using only a single solvent as mobile phase⁴. This method reduces the number of solvent signals which need to be suppressed by ¹H-NMR. It also reduces the time significantly to obtain critical conditions. Using LCCC-NMR onflow experiments, the determination of the true chemical composition distribution and the true molar mass distribution could be achieved via a complete analysis of the microstructure distribution during elution. The microstructure of both the PI and the PMMA block was determined during the chromatographic separation.

Recently, we also developed a LCCC method to separate polyisoprenes (PI) according to their microstructure. LCCC-NMR onflow experiments could verify the structure of the isomeric compounds. It was possible to differentiate between 1,2-, 1,4- and 3,4-PI.

For the first time, an online HPLC-²H-NMR experiment was carried out at deuterated block copolymers. The possibilities for the analysis of block copolymers using deuterium NMR as the detector will be presented. Onflow and stop flow data will be shown.

¹W. Hiller, A. Brüll, D. Argyropoulos, E. Hoffmann, H. Pasch: *Magn. Reson. Chem.*, **2005**, 43, 729-735.

²W. Hiller, P. Sinha, H. Pasch: *Macromol. Chem. Phys.* **2007**, 208, 1965-1978.

³W. Hiller, P. Sinha, H. Pasch: *Macromol. Chem. Phys.* **2009**, 210, 605-613.

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