Comprehensive characterization of branched polymers

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Citation for published version (APA):

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Download date: 30 Jan 2020
Summary

Branched polymers are different from other polymers in many different ways. Due to their structure and properties branched polymers present a challenging class of materials for structural analysis. The main goal of project CoBra (viz. ‘Comprehensive characterization of Branched polymers’) has been the development of new analytical technologies and methodology for branched polymers. Traditional characterization techniques fail to separate long-chain-branched from linear polymers and do not discriminate between the effects of degree of branching and topology. The approach followed in the work described in this thesis has been the exploration and detailed study of separations with unique selectivity towards branched polymers. The emphasis has been on hydrodynamic separations and molecular-topology fractionation (MTF) for high-molar-mass linear and long-chain-branching polymers. Comprehensive two-dimensional separations have been used extensively with combinations of both new and conventional separation modes. These experiments were used to improve understanding of topology-sensitive separations, as well as experimental optimization ultimately resulting in highly-selective separation of branched polymers.

The background of polymer structure and the importance of branching on material properties are presented in chapter 1. A broad overview of different branched polymers and their applications is provided. Classification of branched polymers is based on molecular structure. Topology and branch length together determine the kind of branching, as well as the impact on material properties. Common characterization techniques for different kinds of branching are presented. The overview serves to illustrate that the analytical needs for polymers with highly-abundant branching or low molar masses can be properly addressed using the available characterization techniques. Limitations with respect to conventional characterization of long-chain-branched polymers and the distinct impact of even low levels of branching on rheology provide the main drivers for the work presented in this thesis.
In chapter 2 the preparation of monolithic columns and their application for polymer separations is described. It was verified that columns could be obtained with well-defined and uniform flow-through pores. The application of such stationary phases was of high interest for the studies of topology-selective separations, because these separations require flow-through channels with dimensions comparable to the size of analyte molecules. Flow-resistance measurements and mercury-intrusion porosimetry were performed to obtain accurate pore-size information. Based on these results and the observed polymer separations it was concluded that the prevailing separation mechanism was hydrodynamic chromatography (HDC).

The first demonstration of a comprehensive two-dimensional separation for high-molar-mass polymers with identical size, but different topology is presented in chapter 3. Branching-selective separation was performed on an MTF column with polydisperse sub-1-µm particles. The calibration curve for this column (established using one-dimensional separations) showed reversal of the calibration curve analogous to HDC. In an MTF×SEC experiment (comprehensive two-dimensional liquid chromatography with MTF in the first and size-exclusion chromatography in the second dimension) the branching selectivity in MTF was confirmed, although the effects of size and topology remained confounded. Another important step forward in branching-selective separation demonstrated in this chapter is the separation of a long-chain-branched polymer with a broad molar-mass distribution. The need for MTF columns with well-defined porous properties is highlighted by this work, because accurate statements on the separation mechanism were hindered by the ill-defined nature of the interstitial-channels in a bed with polydisperse particles.

State-of-the-art separations of branched polymers in chapter 4 are the result of progress made in terms of both column technology and understanding of polymer separations in monoliths with extremely narrow flow-through channels. Monoliths described in chapter 2 were used in a systematic study of experimental conditions, such as pore size, flow rate, and hydrodynamic size and topology of analyte polymers. An overview is presented of different separation modes for random-coil polymers in terms of the aspect ratio (λ) and Deborah numbers. The analogy between HDC to MTF at low flow rates and deviations at higher flows are studied using comprehensive MTF×SEC. The
occurrence of ‘critical conditions’, where the non-equilibrium deformation of polymers and retardation effects at high $\lambda$ cancel out, is recognized as a means to enhance the applicability of MTF separations. Within the relatively narrow window of $0.4 < \lambda < 0.9$ the separation of linear from branched polymers is demonstrated for materials with different branching topology.

In chapter 5 the preparation and characterization of well-defined star polymers is described. Reversible addition-fragmentation chain transfer (RAFT) polymerization is a living polymerization. Star polymers can be created with a pre-defined number of arms using multi-functional RAFT agents, provided that suitable leaving groups are used. Mixtures of linear and star polymers were prepared with the linear segments or ‘arms’ all having the same degree of polymerization. The bi-modal molar-mass distribution of the product served as a well-defined star polymer with an internal linear reference. The viscosity contraction ratio was indirectly used to calculate correction factors for SEC separations calibrated with linear polymers. Results of the study were validated against externally published work and against accurate molar masses determined using triple-detection SEC.