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# Branched-polymer separations using comprehensive two-dimensional molecular-topology fractionation × size-exclusion chromatography

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## ABSTRACT

Branching has a strong influence on the processability and properties of polymers. However, the accurate characterization of branched polymers is genuinely difficult. Branched molecules of a certain molecular weight exhibit the same hydrodynamic volumes as linear molecules of substantially lower weights. Therefore, separation by size-exclusion chromatography (SEC), will result in the co-elution of molecules with different molecular weights and branching characteristics. Chromatographic separation of the polymer molecules in sub-μm channels, known as molecular-topology fractionation (MTF), may provide a better separation based on topological differences among sample molecules. MTF elution volumes depend on both the topology and molar mass. Therefore co-elution of branched molecules with linear molecules of lower molar mass may also occur in this separation. Because SEC and MTF exhibit significantly different selectivity, the best and clearest separations can be achieved by combining the two techniques in a comprehensive two-dimensional (MTF × SEC) separation system. In this work such a system has been used to demonstrate branching-selective separations of star branched polymers and of randomly long-chain-branched polymers. Star-shaped polymers were separated from linear polymers above a column-dependent molecular weight or size.

## 1. Introduction

Knowledge of the relationships between polymerization conditions and functional properties of the polymers being formed enables polymer chemists to make materials that are largely optimized for their application. High-performance polymers meet specific needs in the market place. The desired properties of such polymers are typically achieved by optimizing the parameters of the polymerization process. Such an optimization can be performed much more efficiently when key structural parameters affecting polymer properties are understood. Meaningful structure–property relationships can only be developed if the key structural parameters can be measured. In the case of branched polymers, a more detailed description of branching, beyond a basic estimate of the average number of branch points per molecule, is required. Distributions of the molecular properties must be revealed, which requires that the molecules with different degrees of branching be separated, ideally in combination with selective detection techniques. Knowledge of detailed molecular characteristics and their effect on functional properties will ultimately allow the design of high-performance polymers.

Spectroscopic techniques (*e.g.* Fourier-transform infrared, FTIR, or nuclear magnetic resonance, NMR) and physical measurements (*e.g.* light scattering or viscometry) are used on a routine basis to characterize the overall (or average) molecular structure of polymers. Using hyphenated techniques (typically combinations of a chromatographic separation with one or more spectroscopic or physical methods) more information concerning the distributed properties may be obtained. Size-exclusion chromatography (SEC) with light scattering and/or viscometry detection is commonly used to characterize long-chain branching (LCB) in high molecular weight polymers [1–3]. The characterization of LCB in polymers is of particular interest, because of the influence of LCB on processing properties, such as zero-shear viscosity and melt strength. Branching factors based on the Zimm–Stockmayer theory [4] may be calculated when a linear-polymer (reference) sample with identical chemistry or its Mark–Houwink parameters are available. These can subsequently be converted to branching frequencies if assumptions are made regarding the functionality of the branching points and the average branch length. SEC with selective

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detection is, however, not able to fully characterize branched polymers. Separation by size of the unperturbed chain in solution yields fractions containing molecules with equal hydrodynamic volumes, but with different topologies and molecular weights. This distribution cannot be characterized by selective detection techniques. For example, light scattering only provides the weight-average molecular weight for the ensemble of chains eluting in each SEC fraction. Molecular weight polydispersity at a given SEC elution volume was recently confirmed by comparing selective-detection techniques that yielded different types of molecular weight averages (weight average from light scattering and number average from viscometry [5]). The authors demonstrated that the so-called local polydispersity was affected by the distribution of the degree of branching and the functionality. NMR is an alternative technique for determining the structure and the frequency of branch points, but the technique has some limitations. A high-field instrument is needed to detect and quantify low levels of LCB, but discrimination of different branch lengths is still not possible when branches are longer than a few carbon atoms [6]. Most importantly, NMR provides only an average number of branches per molecule.

Multi-dimensional separations can be used to study complex polymers that feature more than one distribution simultaneously. In a comprehensive two-dimensional separation system, denoted by the "×" sign, every part of the sample is subjected to two independent mechanisms and the separation obtained in the first dimension is maintained in the final two-dimensional chromatogram [7]. The peak capacity is increased substantially by comprehensive operation of multi-dimensional separations. However, the separation power is only used efficiently when different selectivity in each separation dimension allows the sample to be separated among its distributions of interest [8,9]. Only in orthogonal separations the retention times in the different dimensions are by definition completely independent (uncorrelated). Although most multi-dimensional separation systems are not orthogonal, confounded distributions that remain unresolved in a single separation step can be separated using two independent separations with different selectivity. Therefore, complex polymers with distributions in distinct molecular properties can successfully be resolved using multi-dimensional systems. Separations by functionality [10] and chemical composition [11] have, for example, been combined with separations according to size using SEC to fully elucidate two mutually dependent distributions.

Branched polymers can also be separated using combinations of independent separations, such as interactive liquid chromatography and SEC, in a comprehensive two-dimensional setup. Selectivity for branched *versus* linear polymers has resulted from differences in the number of repeat units, number of branch points or size in solution. Star polymers prepared by coupling living polystyrene anions were separated by an off-line combination of temperature-gradient interaction chromatography (TGIC) and SEC [12]. The TGIC separation is thought to be based on molecular weight, while SEC is based on the size of molecules in solution. The relationships between molecular weight and hydrodynamic volume are different for branched and linear polymers allowing separations of differently branched polymers by a combination of both methods. Similar star polymers of lower molecular weights were separated on-line by liquid chromatography at the critical composition in combination with either SEC or TGIC (LCCC × SEC or TGIC × LCCC [13]). In the LCCC separation, branched polymers were separated by interaction of the apolar side-groups at the coupling agent. The techniques described here yielded good separations for branched homo-polymers with numerous branches and chemically different branch points or end groups. High molecular weight polymers, with very little long-chain branching, or without functional groups at the branch points or chain ends of different polarity cannot be separated using these techniques.

For LCB polymers, complete separation may be obtained when the polymer is also separated based on branching parameters. Such a separation has previously been demonstrated on monolithic columns containing sub-micron macro pores [14] and on columns packed with sub-micron particles [15]. Both separation systems featured sub-micron flow channels. Polymers above a stationary-phase-dependent molecular weight become retained at low flow rates. Branched polymers were found to elute much later than linear ones of the same molecular weight. This separation method was termed molecular-topology fractionation (MTF) and it was thought to result from the topology-dependent relaxation-time spectrum of polymers in dilute solution [15]. The word topology reflects the geometrical structure of the polymer molecules, more specifically the branch length, frequency and functionality of the branch points. Separation of branched polymers by MTF can only be applied to samples with very narrow molecular weight distributions (MWDs), since the degree of polymerization also affects the retention. Off-line fractionation of LCB polymer by SEC and re-injection of the fractions in MTF was used to demonstrate the differences in selectivity of the two techniques for LCB polymers [15]. Similar to the comprehensive two-dimensional separation systems (described in the previous paragraph) for separating star polymers, samples featuring LCB could be resolved when the separation dimensions display significantly different selectivity towards long-chain branching and hydrodynamic size.

In this paper, the separation of long-chain-branched polymers using MTF × SEC will be demonstrated. Knowledge of the relationship between molecular weight, hydrodynamic size and branching will be used to interpret the selectivity in MTF separations. The separation of polymers with similar hydrodynamic size, but different topologies is demonstrated for star polymers with narrow molecular weight distributions. Results on the separation of randomly long-chain-branched polymers and star polymers will be used to discuss the selectivity of MTF and the applicability MTF × SEC for the separation of complex samples of branched polymers.

## 2. Experimental

### 2.1. Samples and materials

The eluent for MTF and SEC separations was non-stabilized HPLC-grade tetrahydrofuran (THF; Biosolve, Valkenswaard, The Netherlands); it was continuously degassed by purging with helium 5.0 (99.999% Praxair, Vlaardingen, The Netherlands). Sample polymers were dissolved in HPLC-grade THF stabilized with 250 ppm butyl-hydroxylated toluene to prevent degradation by radicals. Narrowly distributed linear polystyrene standards (Polymer Labs., Church Stretton, UK) were used to study retention behaviour. These standards were dissolved at concentrations of 0.5 mg/mL. A nominal three-arm star polystyrene sample was obtained from Polymer Source (Dorval, Canada) and used at a concentration of 1.0 mg/mL. This star polymer was synthesized by coupling of anionically polymerized arms with a tri-functional agent ($\alpha,\alpha',\alpha''$-trichloromesitylene). The manufacturer specified a nominal molar mass of 1480 kg/mol for the precursor arms. However, thorough analysis using size-exclusion chromatography with low-angle light scattering and differential viscometry revealed an arm molar mass closer to 1250 kg/mol. The sample composition was determined from the same experiment. Integration of the concentration signal revealed ~5% to be uncoupled precursor, ~45% linear polymer with double the precursor molecular weight and a remainder of three-arm coupling product. A small amount of higher coupling