Two-dimensional chromatographic separation of branched polyesters according to degree of branching and molar mass

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ABSTRACT

Two-dimensional liquid chromatographic separations of blends of silylated linear and hyperbranched polyesters based on 4,4′-hydroxyphenyl-4′-(tert-butylmethylsiloxy)-phenylvaleric acid were performed using solvent gradient interaction chromatography (SGIC) in the first and size exclusion chromatography (SEC) in the second dimension. The blends analyzed varied in the ratio of branched to linear polymer in order to investigate the potential of the proposed method. The chromatographic experiments proved the capability of two-dimensional chromatography to simultaneously separate polymers according to their topology and molar mass. Baseline separation of high molar mass linear and branched polymers was achieved. The two-dimensional separations for the first time allowed reasonably estimating the amount of statistically branched structures in a matrix of linear ones.

1. Introduction

In the last decade branched polymers attracted increasingly attention from both the scientific and the commercial point of view. The reasons for this development are manifold, e.g. the differences in rheological and mechanical properties of branched structures when compared to their linear analogue. Branching can be a valuable tool to control processability and flow performance of polymers [1]. Another advantage is the high number of functional groups incorporated into the polymer at a rather low synthetic effort. Comparable high numbers of functional groups can also be found in dendrimers, the synthesis of which, however, requires laborious multi-step reactions. Despite the rapidly growing interest in branched polymers, their detailed characterization still presents a major challenge.

Nuclear magnetic resonance spectroscopy (NMR) is frequently applied to quantify the average degree of branching (DB) of polymers. Because in long chain branched polymers the number of branchpoints is very low, application of NMR for DB determination is limited [2]. Most importantly, however, no information on the distribution of branch points among the molecules and therefore on the extent of topological heterogeneity is obtained.

Another common approach to characterize branched polymers is based on the reduced molecular size of branched polymers relative to the linear chain of identical chemical structure and molar mass. This size reduction was predicted first by Zimm and Stockmayer [3]. Usually the reduction in size is described by the well known the branching index g defined as:

$$g = \frac{\langle s^2 \rangle_{br}}{\langle s^2 \rangle_{lin}} \tag{1}$$

Here $\langle s^2 \rangle$ is the mean squared radius of gyration, and the subscripts *br* and *lin* refer to the branched and linear polymers at the same molar mass, respectively. Because branching reduces the coil dimensions, g is always lower than unity. Based on the Zimm–Stockmayer approach, g values were derived for different topologies based on the assumption of random flight subchains [4–9]. The Zimm-Stockmayer approach allows calculating the number of branchpoints based on the experimentally determined branching indices, assuming a given topology.

Similarly, the decrease of intrinsic viscosity of a branched molecule relative to the corresponding linear counterpart can be used to describe the extent of branching. In analogy to g, a branching index g′ can be defined as the ratio of the intrinsic viscosities of the linear and branched sample having the same molar

mass [10–12].

$$g\prime = \frac{\langle\eta\rangle_{br}}{\langle\eta\rangle_{lin}}. \tag{2}$$

Because the determination of g requires quite high molar masses in order to derive the mean squared radius with sufficient accuracy, g′ is often used at lower molar masses. However, relating g′-values to a given structure is more complicated due to the differences to calculate hydrodynamic properties. Therefore, it is advantageous to relate the easier measured g′ values to g. g and g′ are related by

$$g\prime = g^{\varepsilon} \tag{3}$$

where ε is a constant, the value of which depends on the model chosen and on solvent quality. Based on the Flory-Fox-theory a value of $\varepsilon = 3/2$ is expected [13]. Zimm predicted a value of $\varepsilon = 0.5$ for star shaped polymers [10], while empirically values between 0.5 and 1.5 were found [14–16]. For randomly branched polymers, strong variations in the scaling factor ε have been observed, depending on the chemical structure and molar mass of the investigated polymer [17,18]. Once ε is known and g′ has been determined, the number of branches per molecule can be calculated for various branched topologies based on published equations [3,5,9]. However, a simple power law seems to be inadequate to describe the relation between g and g′ [11,16,17].

Another problem in the characterization using the size reduction of branched polymers results from molar mass heterogeneity inherent in any polymer sample. g and g′ relate to the size reduction at identical molar mass. Therefore, the question arises which molar mass average to choose for a heterogeneous sample in order to compare mean squared radii of gyration or intrinsic viscosities at the same molar mass. To overcome this complication g- or g′-values are often determined by coupling SEC with MALLS and/or viscosity detection [14,19–22], assuming homogenous slices at a given elution volume. But even this approach has certain limitations. Often suitable linear analogues, required for calculating g or g′, are not available. In addition, the theoretical treatment to calculate g-values is based on Gaussian subchains, corresponding strictly to theta conditions, while good solvent are typically applied in SEC. Finally, the determination of g or g′ using SEC assumes fractions homogeneous with respect to molar mass at a given elution volume. However, since branched polymers in general possess heterogeneities in both molar mass and topology, coelution of polymers having the same hydrodynamic volumes, but different topologies and therefore different molar masses occurs. The results obtained for molar mass, radius of gyration or intrinsic viscosity at a given SEC-elution volume are therefore again average values [23]. An approach to gain information on the extend of heterogeneity within a SEC-slice utilizes the fact that SEC with viscometry detection yields a local number average molar mass [24], while light scattering detection results in a local weight average molar mass. Thus, by applying both detection systems, determination of the local molar mass dispersity arising from coelution of polymers differing in molar mass should be possible, in principle [23]. Also model calculations were performed to gain information on the extend of heterogeneity resulting from coeluting different topologies [25]. However, these approaches cannot overcome the principal problem of coelution of different molecular species. In order to overcome this fundamental problem, it is necessary to separate effectively linear and branched structures from each other.

Gerber et al. [26,27] showed that two-dimensional chromatography is capable of separating mixtures of linear and star-shaped polystyrenes using a combination of temperature gradient interaction chromatography (TGIC) and SEC. Under the conditions chosen, the separation in TGIC was based mainly on molar mass and only weakly influenced by the architecture of the macromolecules. Thus, TGIC-fractions, nearly homogenous in molar mass, but heterogeneous in architecture, were further separated by SEC into individual peaks for the linear and the branched species, respectively, since at a given molar mass both structures differ in hydrodynamic volume.

Im et al. applied two-dimensional chromatography to linear and statistically branched polystyrenes [28]. Reversed-phase temperature gradient interaction chromatography (RP-TGIC) were performed in the first dimension resulting in a highly efficient separation according to molar mass, since RP-TGIC is supposed to be less influenced by topology than conventional SEC. In the second dimension, critical conditions for linear polystyrene were applied. Under critical conditions the contribution of molar mass on elution volume vanishes and all non-functionalized linear polystyrenes elute at the same elution volume, irrespective of their molar mass. If the polymer chains contain structural units differing in interaction energy from the repeating units, a separation according to those structural units can occur. Since in the study the branchpoints were introduced by dimethylsilylstyrene units, the interaction energy of the branchpoints differed from that of the repeating units, allowing separation according to the number of branchpoints in the second dimension. However, although a separation according to the number of branches was realized, the separation was based on the differences in interaction strength of the branchpoints rather than on topology. Similar holds true for the two-dimensional separation of PLA star polymers by two dimensional chromatography reported by Pasch et al. [29]. Using the difference in interaction energy of OH-groups at the arms, the star polymers were first separated by LCCC according to the number of arms. In the second dimension a separation by SEC was performed. Polystyrene comb polymers were separated by two dimensional chromatography, utilizing isotope effects, since the materials were synthesized with deuterated side chains [30].

Meunier and Edam reported on the chromatographic separation of branched and linear polystyrene molecules of very high molar mass by a new separation technique named molecular-topology fractionation (MTF) [31–33]. These separations utilized columns with sub-micron flow channels. For molecules having dimensions in the order of the channel size, the channels form a tortuous path for the molecules. At very low flow rates macromolecules above a certain size were retarded, with the retention of the branched polymers being more affected than that of the corresponding linear molecules of the same molar mass. Using this approach it was possible to separate very high molar mass narrowly distributed star-shaped polystyrenes polymers from linear ones in a two-dimensional chromatographic separation.

In a previous publication we have studied the retention behaviour of linear and branched polyesters in liquid interaction chromatography [34]. It was shown that at critical conditions of the linear polyester, the branched samples were more strongly retarded. The retention volumes thereby increased with degree of branching (DB). At the same time, at a given DB the retention in LCCC increased strongly with molar mass for the branched polymers, resulting in incomplete recovery at high molar masses. The stronger retention of the branched polymers was also confirmed in gradient elution, where for high molar masses a separation purely based on DB was realized. At lower molar masses retention was influenced by both molar mass and DB. Therefore, separating samples heterogeneous in both, molar mass and DB, requires application of two-dimensional separation methods.

To the best of the authors knowledge, two-dimensional chromatography has not yet been applied for the separation of mixtures