

Separation of branched polystyrene by comprehensive two-dimensional liquid chromatography

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Abstract

Branched polystyrenes (PS) featuring a bivariate distribution in the molecular weight and in the number of branches were characterized by comprehensive two-dimensional liquid chromatography (2D-LC). The branched PS were prepared by anionic polymerization using *n*-butyl Li as an initiator and a subsequent linking reaction with *p*-(chlorodimethylsilyl)styrene (CDMSS). The *n*-butyl Li initiator yields polystyryl anions with broad molecular weight distribution (MWD) and the linking reaction with CDMSS yields branched PS with different number of branches. For the first dimension (1st-D) separation, reversed-phase temperature gradient interaction chromatography (RP-TGIC) was employed to separate the branched polymer according to mainly the molecular weight. In the second dimension (2nd-D) separation, the effluents from the RP-TGIC separation are subjected to liquid chromatography at chromatographic critical conditions (LCCC), in which the separation was carried out at the critical condition of linear homo-PS to separate the branched PS in terms of the number of branches. The 2D-LC resolution of RP-TGIC × LCCC combination worked better than the common LCCC × size-exclusion chromatography (SEC) configuration due to the higher resolution of RP-TGIC in molecular weight than SEC. Furthermore, by virtue of using the same eluent in RP-TGIC and LCCC (only the column temperature is different), RP-TGIC × LCCC separation is free from possible ‘break through’ and large system peak problems. This type of 2D-LC separation could be utilized efficiently for the analysis of branched polymers with branching units distinguishable by LC separation.

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1. Introduction

Liquid chromatography (LC) is a powerful tool for the molecular characterization of polymers that often have multivariate distribution in molecular characteristics such as molecular weight, chain architecture, chemical composition, and functionality [1–8]. The LC separation of polymers can be largely divided into three different modes: the size exclusion mode, the critical condition mode, and the interaction mode. Size-exclusion chromatography (SEC) is the most widely employed technique in the molecular characterization of polymers due to its high speed, facility to use, and wide applicability [1]. Owing to the separation mechanism of size exclusion, however, SEC has an intrinsic limitation. SEC cannot distinguish polymers of the same hydro-

dynamic size but with differences in various molecular characteristics such as composition, chain architecture, microstructure, functionality and so on. Nonetheless, due to the lack of better methods, SEC has been the most popular method for the polymer analysis of various heterogeneities and long chain branching has been characterized by SEC separation combined with light scattering and/or viscometry detection [9,10]. The average number of branches can be estimated according to the method of Zimm and Stockmayer from the molecular weight and the size of the polymers in the SEC fraction determined by light scattering and viscometry detection [11]. The analysis scheme is based on the assumption that the fractions of the SEC effluents are homogeneous in molecular weight and branch number, which is certainly not correct.

Unlike SEC, interaction chromatography utilizes the interactions between polymer segments and the stationary phase, and the molecular weight resolution of interaction chromatography is not much affected by the chain architecture [12]. Interaction

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chromatography was successfully employed to characterize a few model branched polymers such as star shaped polymers [12,13], H-shaped polymers [14], mikto-arm star block copolymers [15,16], and hyper-branched polymers [17]. These model branched polymers were prepared by linking precursor polymers with a narrow distribution in molecular weight. Therefore, the number of branches is proportional to the molecular weight and interaction chromatography was able to separate them in terms of the branch number far better than SEC. This is due to the fact that TGIC separates not with respect to hydrodynamic size but with respect to molecular weight. However, most of the branched polymers in practical use have distributions in both branch molecular weight and number of branches. Accordingly, for the analysis of the polymers having a bivariate distribution, a new method must be devised to obtain the information on branch number distribution as well as molecular weight distribution (MWD). For such an analysis, two-dimensional liquid chromatography (2D-LC) is a natural choice if each LC separation can separate the polymers according to one type of distribution independent of the other. The type of LC for the first and the second dimension separations needs to be chosen to maximize the resolution of the bivariate distribution. The best configuration of a 2D-LC separation is to find chromatographic methods exclusively sensitive to one of the two molecular characteristics while suppressing the effect of the other so that each separation becomes orthogonal to each other [18].

2D-LC has been used for many years to characterize synthetic polymers, biomolecules and complex mixtures [5,19–31]. In the comprehensive 2D-LC setup, a switching valve equipped with two loops was used in a symmetrical configuration. While one loop is being filled with the 1st-D effluent, the fraction that was previously collected in the other loop is analyzed in the 2nd-D separation. The collection time of each fraction in the 1st-D separation has to be equal to or longer than the analysis time in the 2nd-D separation. As a consequence, the analysis time in the 2nd-D separation and the loop volume together determine the flow rate for the 1st-D separation. The total analysis time is essentially the product of the analysis time of the 2nd-D separation and the number of fractions collected from the 1st-D separation. Therefore, to reduce the total analysis time and to keep the 1st-D separation efficiency from the aggravation due to the slow elution, it is imperative to keep the 2nd-D separation fast.

The common configuration of 2D-LC in the analysis of copolymers or functional polymers has been interaction chromatography or LC at critical conditions (LCCC) as the 1st-D to separate in terms of the molecular characteristics other than the molecular weight, mainly the composition or functionality, and SEC as the 2nd-D to separate according to the molecular weight [4,25,28,30,32]. SEC has been a preferred choice for the 2nd-D separation of polymers since SEC is a universal technique to separate polymers according to the molecular size. The SEC retention is seriously affected by molecular characteristics other than molecular weight, but once homogeneity of the sample is achieved after the 1st-D separation, the SEC retention is more meaningfully correlated with the molecular weight. Furthermore, with the development of new type of

columns, SEC separation can be carried out fast in a few minutes [33].

In this work, we demonstrate the use of a comprehensive 2D-LC method to separate branched polystyrenes (PS) according to both molecular weight and branch number.

2. Experimental

2.1. Preparation of branched polystyrenes

The branched PS were prepared by linking polystyryl anion precursors with 4-chlorodimethylsilylstyrene (CDMSS) [34]. CDMSS was prepared following the literature procedure [35] and stored at -25°C in a dry box filled with Ar gas. *n*-Butyl Li (2.0 M solution in cyclohexane), cyclohexane (anhydrous, 99.5%), and styrene (99%) were purchased from Aldrich. Tetrahydrofuran (THF) and methanol were purchased from Merck (HPLC grade). Styrene was distilled from calcium hydride under reduced pressure. THF and cyclohexane were distilled from sodiobenzophenone. Styrene, THF, cyclohexane, and methanol were transferred into a dry box filled with argon gas and purified again by passing through a column filled with activated neutral alumina (Merck, 70–230 mesh) that was baked at 250°C for 24 h in vacuo. Purified styrene was stored at -25°C in the dry box.

Polystyryl anions were prepared by adding *n*-butyl Li 2.55 mL (5.09 mmol) to a solution of cyclohexane 105 mL, styrene 10.5 mL and THF 284 μL under Ar atmosphere at 25°C . The polymerization mixture was stirred for 30 min at 25°C and three portions of 38 mL solution were transferred to three flasks. One of the separated solutions of polystyryl lithium was terminated with methanol to obtain the precursor PS and the other two portions were treated with CDMSS at the CDMSS/living end molar ratios of 0.49 (162.5 μL , BS49), and 0.65 (216.6 μL , BS65) at 25°C . After allowing the reaction to proceed for 3 h, the reaction mixtures were terminated by adding a small amount of methanol. The PS was precipitated by dropping the reaction mixture into a large excess of methanol and the precipitated PS was collected by filtration and dried at 60°C under vacuum. The scheme of the coupling reaction with CDMSS is shown in Fig. 1.

2.2. SEC analysis

For the SEC analysis, two mixed bed columns (Polymer Labs., PLgel Mixed-C, 300 mm \times 7.5 mm) were used at a column temperature of 40°C . SEC chromatograms were detected with a multi-angle laser light scattering (MALLS, Wyatt, mini-DAWN) at a wavelength of 690 nm and a refractive index detector (Wyatt, Optilab DSP) using THF (Samchun, HPLC grade) as the eluent at a flow rate of 0.8 mL/min. Polymer samples for the SEC analysis were dissolved in THF at a concentration of ca. 1.0 mg/mL and the injection volume was 100 μL .

2.3. RP-TGIC and LCCC analysis

For the RP-TGIC separation, a C18 bonded silica column (Kromasil C18, 100 \AA , 150 mm \times 4.6 mm) was used. The mobile

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