Short Metal Capillary Columns Packed with Polymer-Coated Fibrous Materials in High-Temperature Gas Chromatography

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Abstract

The high-temperature gas chromatographic (GC) separation of several semivolatile compounds is studied with a short metal capillary column packed with fibrous material, having a polydimethylsiloxane coating thereon. Taking advantage of the excellent heat-resistance of the fiber and also the combination of the surface-deactivated metal capillary, a temperature-programmed separation up to 450°C is successfully demonstrated for the separation of polymer standard samples. The average molecular weight of the commercially-available polymer standard samples for size exclusion chromatography (SEC) is estimated by high-temperature GC analysis and compared with the nominal value determined by a conventional SEC method. Although a slight deviation for the number-average molecular weight is observed between the GC and SEC analysis, the data for the weight-average molecular weight shows a good agreement in these methods. The results also suggest the future possibility of the fiber-packed metal capillary as a miniaturized GC column with an increased sample loading capacity.

Introduction

During the past several decades, continuous efforts have been made to develop a novel separation column for gas chromatography (GC), and open-tubular capillary columns have been successfully applied for separating a wide variety of volatile compounds (1). However, the conventional packed columns are still employed in the routine separations of a certain class of compounds. Various types of stationary phases were developed along with the subsequent commercialization. However, only a limited number of publications have been reported for the employment of fibrous stationary phases, except for the characterization of the fibrous polymer itself in an inverse gas chromatography (IGC) method, in which the surface of the fibrous packing materials was analyzed based on the interaction with the standard solutes (2–4). The basic concept of the IGC techniques suggests that the fibrous polymer could be introduced as a stationary phase if one can control the separation conditions, such as temperature program, carrier-gas flow rate, and the surface of the fiber.

Several synthetic fibers have been introduced as a novel material in miniaturized sample preparation (5–15) and chromatographic separations (16–20). Taking advantage of the excellent stability for typical organic solvents commonly employed in the sample preparation and subsequent liquid phase separation techniques, a miniaturized sample preparation method was developed (5–7) along with the effective on-line coupling with microscale separations such as: microcolumn liquid chromatography (micro-LC) (8–12), capillary electrochromatography (13,14), and capillary electrophoresis (13,15). Compared with a conventional solid-phase extraction cartridge packed with a spherical particle, such as octadecylsilica, the fiber-packed extraction cartridge showed both an improved permeability and increased sample loading capacity. This allows the downsizing of the extraction device, and has the significant benefit of repeatable use (6,8). Another advantageous feature is the availability of various types of synthetic fibers with different chemical structures and the polymeric materials for the coating thereon. The selectivity for the extraction could be tuned by selecting an appropriate coating for the fiber surface (7–10).

On the basis of the successful use of those fibrous materials described previously, several types of heat-resistant fibers have been introduced as the novel stationary phase in packed-capillary GC (18–20). A bundle of filaments was longitudinally packed into a fused-silica capillary having a typical length of 1 to 2 m. In contrast to the particle-packed capillary columns, the fiber-packed columns exhibited quite a low pressure drop because the parallel alignment of those filaments effectively keeps the channels opened through the column for the flow of the carrier gas. Polymer coating on the fiber surface was also studied. Coated with the conventional polysiloxane-based liquid phases for an open-tubular capillary GC column, the surface of

the packed filaments was successfully modified, and the separation characteristics (such as retentivity and selectivity) have been designed for the separation of a particular class of compounds. The increased sample loading capacity is another advantageous feature of polymer-coated fiber-packed capillary columns.

In this work, a deactivated metal capillary was introduced as the column material, and high-temperature GC separations were studied with polymer-coated fiber-packed metal capillary columns. As one of the column materials, metal capillary has been studied by many research groups, and the importance of the deactivation has also been discussed. Among the developed methods, the deactivation of the inner surface of the metal capillary in this work was based on silica-layer formation by pyrolyzing perhydropolysilazane (PSZ) (21). After the deactivation process, a bundle of heat-resistant fiber was packed into the metal capillary with a typical size of 0.3-mm i.d. and 1-m length, followed by the polymer-coating process onto the packed filaments as reported earlier (18–20). In order to evaluate the performance of the columns, some standard samples prepared for the molecular weight determination in size exclusion chromatography (SEC) were separated along with commercially available wax materials consisting of a semivolatile alkane mixture.

Experimental

Materials and chemicals

All solvents and sample solutes were of analytical grade and purchased either from Kishida Chemical Co. (Osaka, Japan) or GL Sciences, Inc. (Tokyo, Japan). Zylon, poly(p-phenylene-2,6-benzobisoxazole), was supplied from Toyobo Co. (Shiga, Japan). PSZ was obtained from Clariant Japan Co. (Tokyo, Japan). The chemical structure of Zylon is illustrated in Figure 1 along with a typical photograph of Zylon filaments taken by a scanning electron microscope (Model JSM-5900LV, JEOL, Tokyo, Japan). The diameter of each filament is approximately 11.5 μm.

Deactivation of metal capillary

The metal deactivation process was carried out according to the method of Takeichi et al. (21). Before the deactivation process, the stainless steel capillary (0.30-mm i.d., 0.50-mm o.d., 30 m) (Shinwa Chemical Industries Ltd., Kyoto, Japan) was sequentially washed with 2 mL each of dichloromethane, methanol, water, concentrated hydrochloric acid, water, methanol, and dichloromethane. The metal capillary was then oxidized by passing oxygen through the GC oven. Next, m-xylene solution of PSZ (20%) was passed through the oven, followed by heat treatment at 400°C for 2 h to form the silica layer on the surface. After cooling, the capillary was rinsed with dichloromethane.

Fiber packing and polymer coating

To prepare the fiber-packed columns, a bundle of Zylon filaments (166 ± 2 filaments) was longitudinally packed into the deactivated metal capillary in a similar manner described pre-

viously (9). Typical length of the fiber-packed column was 1 m, unless otherwise specified. To ensure the reproducible preparation of fiber-packed capillary columns, the total number of packed-filaments was precisely counted before and after the packing process.

For the preparation of coated-fiber packings, HR-1 [100%-methyl-polysiloxane and polydimethylsiloxane (PDMS)] (Shinwa Chemical Industries) was used as the coating material. The coating procedure was similar to that described previously (18–20). First, a fiber-packed capillary was connected to the pressure-proof vessel containing 10 mL of acetone and washed with the solvent pumped by N_2 gas at the pressure of 500 kPa. The suitable number of filaments packed for the preparation of the coated fiber-packed capillary was determined by the preliminary experiments. After the same volumes of the solvents (water, acetone, and chloroform) were pumped in a similar manner, the capillary was allowed to dry at room temperature for approximately 2 h using N_2 gas flow. Second, the capillary was subject to heating in a GC oven with the flow of N_2 gas. The temperature was programmed from room temperature to 300°C at 2°C/min and then held for approximately 10 h. Next, the solution of the PDMS (HR-1) coating material (3%) in n-hexane containing a cross-linking reagent (0.8% to the PDMS), benzoyl peroxide, was pumped through the packed capillary. After the total volume of the polymer solution (0.5 mL) was pumped, the N_2 flow was maintained for more than 5 h. Then, the column was installed in the GC oven again, and the programmed heating was carried out as follows: from 40°C to 300°C at 0.5°C/min and then held for more than 48 h to ensure the complete reaction.

The successful fiber-packing and polymer-coating treatments were confirmed by the separation of a standard sample containing three n-alkanes, n-dodecane, n-tetradecane, and n-hexadecane. The relative standard deviations (RSDs) for the retention factors were less than 2.0% on three columns separately prepared with the same coating, where the average
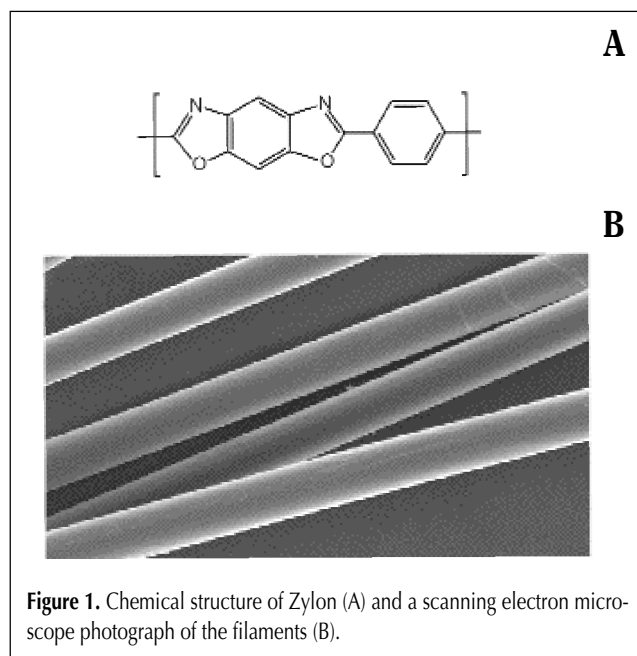
Figure 1. Chemical structure of Zylon (A) and a scanning electron microscope photograph of the filaments (B).

values of the retention factors for three consecutive runs on each column were used for the calculation. The RSDs for multiple injection onto the same column were less than 1.5% (n = 3) for all the columns studied.

GC measurements

A HP 5890-II GC (Yokogawa Analytical Systems, Tokyo, Japan) with a split/splitless injection port and a flame ionization detector (FID) was used for all GC measurements. He or N_2 was used as the carrier gas, and the carrier gas and air were supplied from the respective gas cylinders through a cartridge packed with a molecular sieve (GL Sciences, Inc.). The other separation conditions such as carrier gas flow rate, column head pressure, and temperature programs were determined by the results of preliminary experiments for each sample. The data collection was made with Borwin Chromatography Data Handling Software (Jasco, Tokyo, Japan) on a personal computer.

Results and Discussion

Evaluation of the basic performance

The van Deemter plots on a polymer-coated fiber-packed capillary column are shown in Figure 2. The theoretical plate number was measured for n-butane, and the data points for HETP (the height equivalent to a theoretical plate) were plotted against the linear velocity of each carrier gas. For these measurements, a capillary column of 5-m length, prepared by the same procedure as that for 1-m length, was employed to ensure the precise control of the relatively lower column inlet pressure that corresponds to the linear velocity of less than approximately 5.0 cm/s. As shown, these plots have similar profiles to the results obtained with conventional particle-packed columns, having a typical optimum linear velocity of approxi-
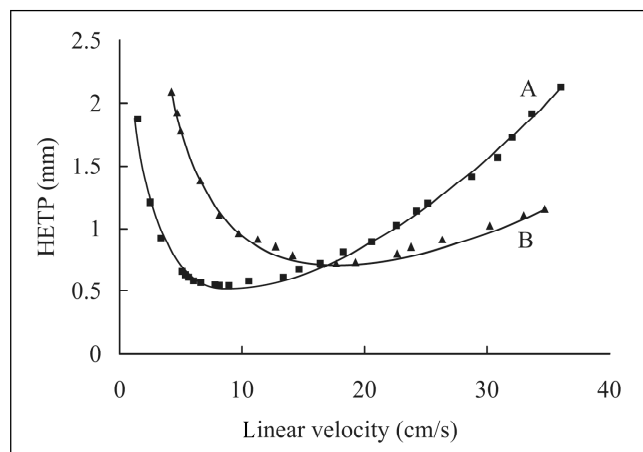
Figure 2. van Deemter plots for n-butane with the polymer-coated fiber-packed column. Conditions: column, deactivated metal capillary (0.3-mm i.d., 5 m) packed with the HR-1 (3%) coated Zylon (166 ± 2 filaments); column temperature, 130°C (isothermal); injector and detector temperature, 200°C and 250°C, respectively. Other conditions are listed in the text. Carrier gas: N_2 (A) and He (B).

mately 8–12 cm/s (22). The minimum HETP value for N_2 carrier gas was 0.54 mm at the linear velocity of 8.9 cm/s, and 0.71 mm at 17.6 cm/s for He. The optimum linear velocity for N_2 corresponded to the head pressure of approximately 10 kPa on the polymer-coated fiber-packed column of 1 m.

In contrast to a limited sample injection volume on typical open-tubular capillary columns, the polymer-coated fiber-packed capillary column has an increased sample loading capacity as described in previous publications (18–20). Taking advantage of the large sample loading capacity, an injection of more than 10 μL is possible even without sample splitting. The higher operation temperature is another merit of the metal capillary column packed with a Zylon fiber, which is a representative of thermally-stable synthetic fibers (19). On the basis of the mentioned advantageous features, the column temperature was elevated up to 450°C in the following experiments. Prior to use, column preconditioning was carried out at the highest scheduled temperature (i.e., 450°C) for more than 30 min; however, no significant bleeding effect was observed for all the columns prepared, suggesting not only a successful coating process but also a good combination of the polymeric liquid phase and the polymeric support material. Those columns showed a long lifetime even for the repeated use with the temperature-programmed operations up to 450°C, though only a slight decrease in the retention time (typically less than 2% for n-alkanes) was observed after 100 repeated runs.

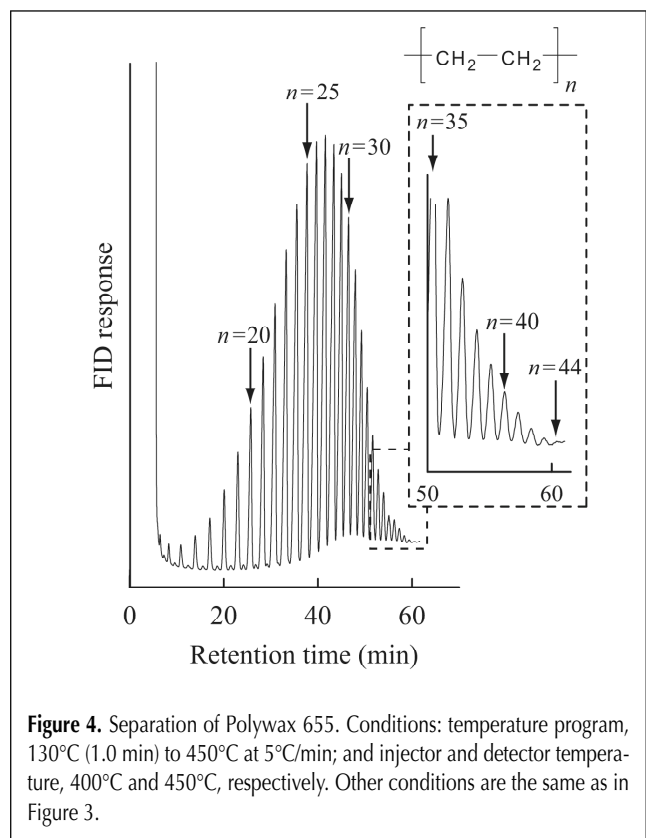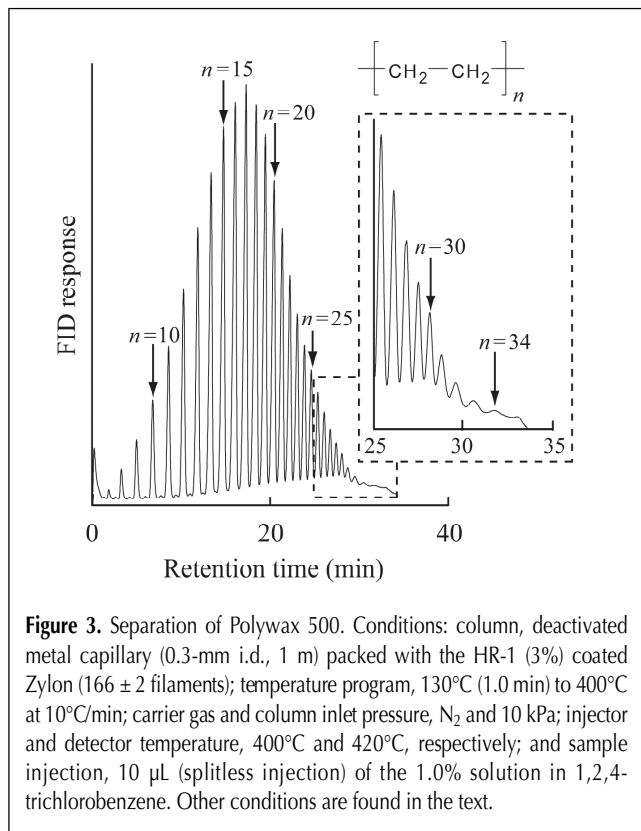### Separation of Polywax samples

Typical chromatogram for the separation of Polywax 500 on the polymer-coated fiber-packed capillary is shown in Figure 3. Because Polywax consists of polyethylenes (PEs) having a range of molecular weights, the carbon number of the last-eluting peak could be determined as 68, corresponding to a molecular weight of more than 950, even if the contribution of the terminal groups is excluded. It can be said that the fiber-packed short metal capillary column has a good separation performance for the mixture of the PEs and a high sample loading capacity. The increased sample loading capacity will be suitable for the separation of a complex mixture in the conventional GC system, typically accompanied with FID as the detector.

As shown in Figure 4, similar good separation was also obtained for Polywax 655, in which the average molecular weight of the constituents was higher than that of Polywax 500. The molecular weight of the last-eluting peak was more than 1200. The results clearly demonstrate the practical separation of these PE mixtures on the short metal capillary column packed with PDMS-coated fibrous material, and also suggest the potential applications for the separation of other semivolatile compounds consisting of many components.

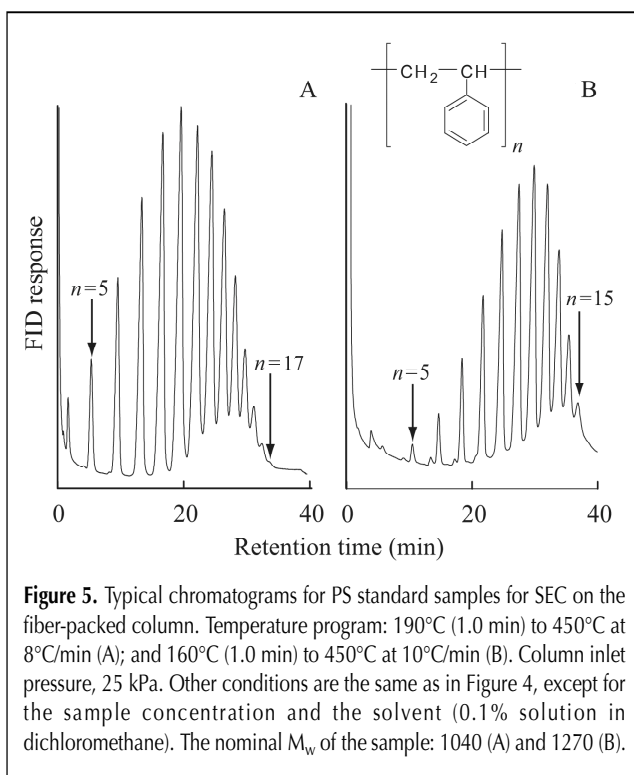### Application to the analysis of SEC standards

On the successful separation of typical polymeric mixtures, further studies have been carried out for the application of the fiber-packed metal capillary column. Figure 5 shows the separations of two polystyrene (PS) standard samples. The PS samples are commercially available as the standard for molecular weight determination in SEC. The nominal average mol-

ecular weights of these standards are (A) 1040 and (B) 1270, in which these average values were determined using SEC by the supplier and expressed as the weight-average molecular weight (M_w) value. The number-average molecular weights (M_n) and

Figure 3. Separation of Polywax 500. Conditions: column, deactivated metal capillary (0.3-mm i.d., 1 m) packed with the HR-1 (3%) coated Zylon (166 ± 2 filaments); temperature program, 130°C (1.0 min) to 400°C at 10°C/min; carrier gas and column inlet pressure, N_2 and 10 kPa; injector and detector temperature, 400°C and 420°C, respectively; and sample injection, 10 µL (splitless injection) of the 1.0% solution in 1,2,4-trichlorobenzene. Other conditions are found in the text.

Figure 4. Separation of Polywax 655. Conditions: temperature program, 130°C (1.0 min) to 450°C at 5°C/min; and injector and detector temperature, 400°C and 450°C, respectively. Other conditions are the same as in Figure 3.

the resulting polydispersity index (calculated as M_w/M_n) for these standard samples are as follows: (A) M_n = 960, M_w/M_n = 1.08 and (B) M_n = 1200, M_w/M_n = 1.06, respectively. As the molecular weight of a polystyrene monomer unit is approximately 104, the molecular weight distributions obtained by the GC analysis should have a good agreement with the M_w value. Because the detection of these separations has been made with FID, the obtained peak area for each peak was assumed to be proportional to the absolute weight of carbon atoms, not to the number of molecules in each peak. Although further optimization should be needed for these separations, especially the improvement of the separation for several peaks eluted later, the results also indicated a further application for other polymer standards. Assuming complete reaction during polymerization, the molecular weight of the last eluting peaks in Figure 5A could be determined as approximately 1828.7 because the terminal groups of each polymer molecule are tert-butyl and hydrogen in this standard sample, as reported by the supplier.

For the separation of poly(methylmethacrylate) (PMMA), a similarly good separation was demonstrated as found in Figure 6. The M_w was determined by the manufacturer with the conventional SEC method and reported as 1150 with a M_w/M_n value of 1.15. Taking into account the FID response of the ester functional groups, and also assuming equal FID response for all monomer units in each polymer molecule, the M_w was estimated with tert-butyl group and hydrogen as the terminal groups. For the calculation, the PMMA sample was also separated with another temperature-programmed run to observe the peaks for PMMA oligomer molecules having the degree of polymerization (n) of less than 6, although contribution of these smaller molecules was insignificant for the calculation. The estimated M_w of approximately 1155 has a good agree-

Figure 5. Typical chromatograms for PS standard samples for SEC on the fiber-packed column. Temperature program: 190°C (1.0 min) to 450°C at 8°C/min (A); and 160°C (1.0 min) to 450°C at 10°C/min (B). Column inlet pressure, 25 kPa. Other conditions are the same as in Figure 4, except for the sample concentration and the solvent (0.1% solution in dichloromethane). The nominal M_w of the sample: 1040 (A) and 1270 (B).
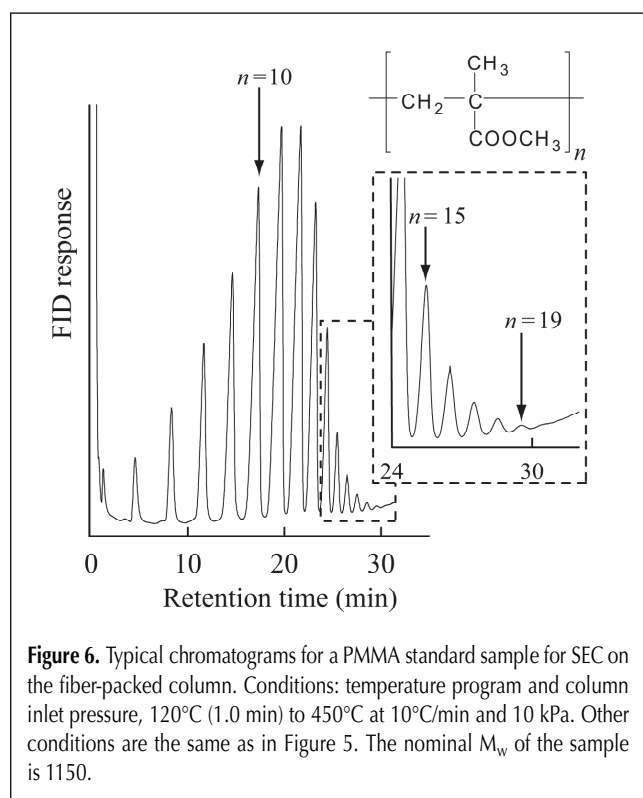
ment with the reported nominal value of 1150, suggesting the successful determination from the peak area in the chromatograms. However, the estimated M_n value (1096) in the GC analysis was somewhat larger than the reported value of 1000, suggesting a deviation from the reported value measured by the SEC method with a refractive index (RI) detector. With similar estimation to that for Figure 5A, the molecular weight of the last-eluting peak in Figure 6 was determined as approximately 1960.3.

Conclusion

Polymer-coated fibrous stationary phase was introduced as the packing material in a short metal capillary column, and the basic separation performance was studied. With the successful combination of the heat-resistant fibrous material and the short metal capillary, high temperature separation of several polymer mixtures has been demonstrated. The estimated average molecular weight in the GC analysis (detected with FID) showed a good agreement with that determined by the conventional SEC method using RI detection.

Although further studies should be necessary for improving the theoretical plate number of the fiber-packed separation column and introducing other types of stationary phases such as surface-modified fibrous material, the results in the present work clearly showed the novel use of the heat-resistant fiber and its applications for the separation of semivolatile compounds. Down-sizing of the GC column will also be possible with fibrous support materials and chemical modification or an appropriate coating thereon (or both).

Figure 6. Typical chromatograms for a PMMA standard sample for SEC on the fiber-packed column. Conditions: temperature program and column inlet pressure, 120°C (1.0 min) to 450°C at 10°C/min and 10 kPa. Other conditions are the same as in Figure 5. The nominal M_w of the sample is 1150.

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