Notes

Determination of Monomer Conversion in Methacrylate-based Polymer Monoliths Fixed in a Capillary Column by Pyrolysis–Gas Chromatography

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Monomer conversion and the resultant copolymer composition of polymer monolith columns are important factors for controlling column characteristics. We propose a new method to determine monomer conversion to a polymer monolith fixed in a capillary column using pyrolysis–gas chromatography. Small pieces of a poly(butyl methacrylate-*co*-ethylene dimethacrylate (BMA-*co*-EDMA)) monolith column were pyrolyzed at 450°C with poly(ethyl methacrylate) as a non-volatile internal standard. The monomer conversions were estimated from the corresponding relative peak intensities in the pyrogram. It was determined that the conversion of EDMA was significantly greater than that of BMA in a low-conversion UV-polymerized poly(BMA-*co*-EDMA) monolithic capillary column.

Introduction

Recently, porous monolithic columns have attracted significant attention in the field of HPLC. The materials used for a monolithic bed are classified into two categories: silica monoliths[1] and polymer monoliths.[2,3] Silica-based monolithic columns have some advantages over polymer-based ones, including a well-controlled pore structure, good mechanical strength, and high column efficiency, especially for small molecules. On the other hand, polymer-based monolithic columns have unique characteristics, such as applicability over a wide pH range and simple preparation. In the last few years, the preparation of polymer monolithic columns *via* low-conversion polymerization has been reported by some research groups.[4–8] In these studies, low monomer conversion often led to a high separation efficiency. These results suggest that a relatively short polymerization period for monolith column preparation might impart superior column efficiency.

In general, monomer conversions are estimated by measuring the amount of unreacted monomers that are flashed out from the column after polymerization.[4–7] However, the exact conversion of the monomers to a monolithic stationary phase in the column cannot be measured using this method, because it does not account for small fragments of polymers that could be washed out from the column. Therefore, an alternative method is required to determine the exact monomer conversions to monolithic structures fixed in capillary columns for further progress in the improvement of polymer monolith columns.

Pyrolysis–gas chromatography (Py-GC) is frequently used for analyses of synthetic polymers, even those that are insoluble.[9,10] In general, polymer monoliths are insoluble cross-linked polymers, and various monomers have been used for the syntheses.[11] Polymethacrylate is one of the most common base materials for polymer monoliths, and it is well-known that methacrylate-based polymers are readily depolymerized to the monomers at elevated temperatures.[12] Therefore, the composition of the methacrylate-based polymer can be determined directly from the peak intensities of the original monomers observed in the pyrogram. Furthermore, the amount of sample required for a Py-GC measurement is quite small (*i.e.*, generally less than 50 μg). Therefore, Py-GC is suitable for the compositional analysis of small amounts of polymer monolith synthesized in a capillary. In this study, we used Py-GC to determine the monomer conversion to methacrylate-based polymer monoliths fixed in a column without any pretreatment.

Experimental

Chemicals

Butyl methacrylate (BMA), ethylene dimethacrylate (EDMA), 1-decanol, cyclohexanol, 2,2-dimethoxyphenyl-2-acetophenone (DMPA), α-α′-azobisisobutyronitrile (AIBN), poly(ethyl methacrylate) (PEMA), methanol, and acetone were purchased from Wako Pure Chemicals (Osaka, Japan). 3-Methacryloxy-propyltrimethoxysilane (MPTS) was obtained from Shin-Etsu Chemicals (Tokyo, Japan). All chemicals were used as received.

Preparation of monolith

Two types of poly(BMA-*co*-EDMA) monolith, *i.e.*, bulk monolith and that formed in a capillary column, were prepared from a reaction solution consisting of BMA (24 wt%), EDMA (16 wt%), 1-decanol (34 wt%), and cyclohexanol (26 wt%).[13] The molar ratio of BMA/EDMA in the reaction solution was 2.08/1. To synthesize the standard bulk monolith, AIBN (1 wt% respect to the total amount of monomers) was added to 1 mL of the reaction solution in a small vial (10 mm i.d.), and the solution was thermally polymerized at 65°C for 24 h. The resultant bulk monolith was washed with methanol to remove unreacted monomers, oligomers, and porogens (*i.e.*, 1-decanol

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and cyclohexanol), dried *in vacuo* for 2 h, and cryomilled for 45 min. Finally, the obtained monolith powder was further washed with methanol and dried *in vacuo* for 2 h.

The capillary monolith columns were prepared by both thermal and photo-initiated polymerization in a fused-silica capillary (0.1 mm i.d.) with an MPTS-modified inner surface.[13] The thermal polymerization conditions were the same as those for the bulk solution. Photo-initiated polymerization (UV 254 nm, 2 mW/cm^2) was performed at low temperature (0°C) for various polymerization periods according to our previously reported method.[13] In this reaction, 1 wt% DMPA with respect to the amount of monomer was added to the reaction solution as photo initiator.

Py-GC measurement

A vertical microfurnace-type pyrolyzer (Frontier Laboratory PY-2020iD) was directly attached to the injection port of a gas chromatograph (G-6000, Hitachi) equipped with a flame ionization detector (FID). The monolith sample and PEMA (2.4 μg) as an internal standard (IS) were placed in a deactivated stainless-steel sample cup, and then introduced into the headed center of the pyrolyzer to depolymerize the poly(BMA-*co*-EDMA) monolith into BMA and EDMA. To analyze the bulk monolith, a weighted amount of the monolith (*ca.* 5 to 30 μg) was pyrolyzed with IS. To analyze the capillary monolith, a 10 ± 0.5 mm sample of the capillary column was cut into three pieces, which were placed in a sample cup with IS, and then dropped into the pyrolyzer to pyrolyze the monolith fixed in the fused-silica capillary (maximum about 30 μg). The Py/GC interface and the injection port of the GC were heated at 280°C to prevent condensation of the pyrolysis products.

For separation of the degradation products, a metal capillary column (Ultra ALLOY$^+$-1701, 30 m × 0.25 mm i.d. × 0.25 μm coated with 14% cyanopropylphenyl–86% dimethylpolysiloxane) was used. A flow rate of 57 mL/min He carrier gas was used to rapidly sweep the pyrolysis products from the pyrolyzer to the separation column. The carrier gas flow was reduced to 1.14 mL/min at the inlet of the capillary column by means of a splitter. The temperature for the column was initially set at 40°C, elevated up to 280°C at a rate of 20°C/min, and then maintained at 280°C for 20 min.

Results and Discussion

Py-GC analysis of monolith

Generally, an IS is used for quantitative analyses. In this study, volatile compounds are not suitable for ISs because volatilization of the standard from a sample cup causes an instability of the analytical result. Therefore, PEMA, which is a methacrylate-based polymer that readily depolymerizes to EMA at elevated temperature, was used as the non-volatile IS for this study. A 4.0-μL aliquot of the standard solution (0.6 μg/μL acetone solution) was added to the sample cup using a microsyringe, and the acetone solvent was evaporated for about 30 s at room temperature before analysis.

Typical pyrograms of poly(BMA-*co*-EDMA) monoliths at 450°C with PEMA as the IS are shown in Fig. 1. The bulk monolith almost exclusively depolymerized into its constituent monomers, *i.e.*, BMA and EDMA, together with EMA from PEMA at 450°C (Fig. 1A). When the pyrolysis temperature was less than 400°C, the pyrogram peaks were slightly broader due to a decreased depolymerization rate. At pyrolysis temperatures above 500°C, undesired fragmentation (over decomposition) of the monolith was observed. Therefore,
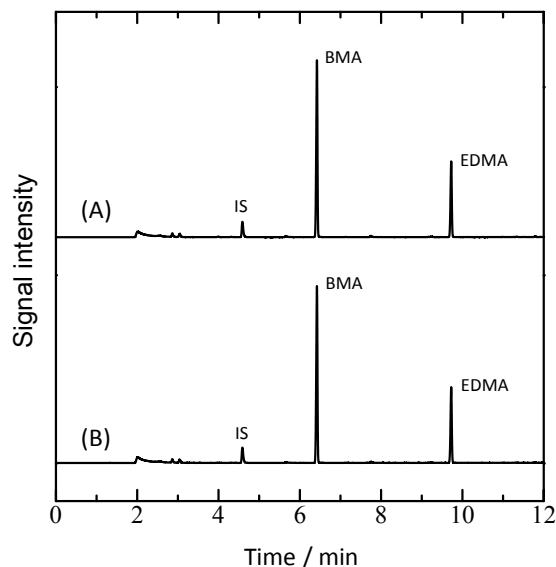

Fig. 1 Pyrograms of poly(BMA-*co*-EDMA) monolith at 450°C. (A) Bulk monolith, 10.1 μg, (B) capillary monolith column prepared at 65°C for 24 h, 10 mm. PEMA (2.4 μg) was added as the IS.

450°C was employed as the pyrolysis temperature. The monolith fixed in the capillary column (0.1 mm i.d. × 10 mm) also decomposed to BMA and EDMA without any pretreatment before pyrolysis, as shown in Fig. 1B. After analyses, no residue was observed in the sample cup or inside the capillary. Almost all monoliths decomposed at the elevated temperature.

In analyses of the 10 mm long capillary monolith column, the repeatabilities of the peak intensities of IS, BMA, and EDMA were 3.3, 3.1, and 2.7% relative standard deviation (RSD; $n = 5$), respectively. The RSD values of the relative peak intensities for BMA/IS, EDMA/IS, and BMA/EDMA were 5.6, 5.3, and 0.7%, respectively. The precision of the yields of the BMA and EDMA monomers relative to the IS was about 5% RSD. The higher precision, *i.e.*, 0.7% RSD for the BMA/EDMA ratio, suggests that polymerization proceeded homogeneously in the capillary column.

Determination of conversion

The monomer conversion in poly(BMA-*co*-EDMA) monolith was assessed based on the amount of monomers produced during pyrolysis. BMA and EDMA were calibrated from the peak areas of the monomers from the bulk monolith relative to those from the IS (*i.e.*, BMA/IS and EDMA/IS) and the corresponding constituents contained in the monolith obtained at various amounts of monolith samples.

First, the copolymer composition of the bulk monolith, *i.e.*, molar ratio of BMA and EDMA, was evaluated using Py-GC. The average peak area ratio of BMA/EDMA from the Py-GC measurements of the bulk monolith was 2.45 ± 0.03 ($n = 6$, with monolith amounts ranging from 5.8 to 23.6 μg). A mixture of BMA and EDMA standard (at a molar ratio of 2.08/1) was then subjected to GC analysis which resulted in a peak-area ratio of 2.16/1. Thus, the molar ratio of the BMA/EDMA composition of the bulk monolith was estimated to be 2.38/1 (1.71/1 in weight ratio).

The calibration curves for BMA and EDMA are shown in Figs. 2A and 2B, respectively. The top axes indicate the amount of bulk monolith used to construct the calibration curves, while the bottom axes correspond to the amounts of BMA or EDMA
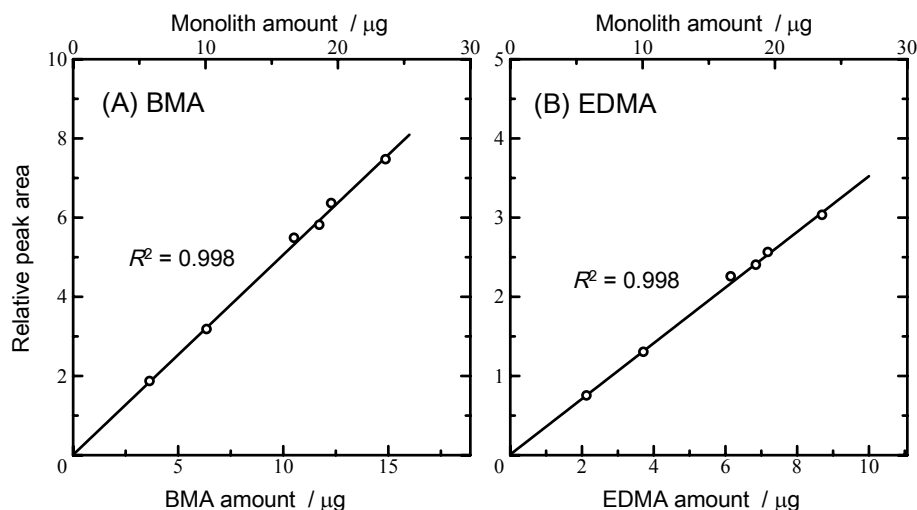
Fig. 2   Calibration curves for (A) BMA and (B) EDMA based on the relationship between the peak areas of the monomers from the bulk monolith relative to that of the IS (*i.e.*, BMA/IS and EDMA/IS) and the corresponding constituents of 5.8 – 23.6 μg monolith samples.

in the monolith, which were estimated using the BMA/EDMA composition of the bulk monolith. The left axes show the peak areas of the depolymerized monomers from the bulk monolith relative to those of the IS (*i.e.*, BMA/IS and EDMA/IS). Good linearity ($R^2 > 0.998$) was obtained in both calibrations, and the monoliths were depolymerized quantitatively in this range. The LODs ($3\sigma/S_a$, where S_a and σ are the slope and the standard deviation of the intercept, respectively) for BMA and EDMA were both 0.08 μg, and the LOQs ($10\sigma/S_a$) were 0.27 μg for BMA and 0.25 μg for EDMA. Using these calibration curves, the amounts of BMA and EDMA produced from the pyrolysis of monolith fixed in a capillary could be determined.

The conversion of the monolith formed in the capillary was then estimated as follows. The volume of the capillary (0.1 mm i.d. × 10 mm) was 78.5 nL, and the density of the reaction solution was 1.08 g/mL at room temperature. The contents of BMA and EDMA in the solution were 24 and 16 wt%, respectively. Thus, 20.3 and 13.6 μg of BMA and EDMA, respectively, were fed into the capillary of 10 mm long. These values should correspond to 100% conversion, meaning that all monomers were converted to monolith in the capillary. Therefore, the conversions (%*C*) were estimated from the following equation:

$$\%C = \frac{\text{Amount of monomer determined by Py-GC of monolith sample}}{\text{Amount of monomer contained in the original solution}} \times 100.$$

Based on the pyrogram shown in Fig. 1B and the calibration curves (Fig. 2), 17.5 ± 1.1 and 11.6 ± 0.7 μg ($n = 5$) of BMA and EDMA, respectively, were obtained from the monolith in the 10 mm column. Therefore, the %*C* values of BMA and EDMA were 86.3 ± 5.4 and $85.7 \pm 5.1\%$, respectively. When the thermal polymerization period was extended from 24 to 36 h, the conversions to the monolith in the capillary reached 103.8% for BMA and 99.8% for EDMA. The monomer conversions to poly(BMA-*co*-EDMA) monolith fixed in a capillary column were determined directly using Py-GC.
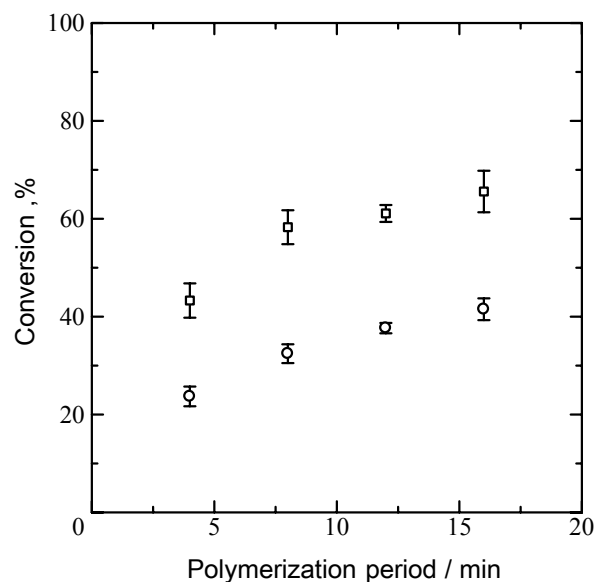

Fig. 3 Relationship between the polymerization period and conversions of BMA (○) and EDMA (□) determined by Py-GC. Sample: UV-polymerized poly(BMA-*co*-EDMA) monolithic column (0.1 mm i.d. × 10 mm). The error bars indicate the standard deviation ($n = 3$).

Relationship between polymerization period and monomer conversions

In our previous report, a poly(BMA-*co*-EDMA) monolithic capillary column was prepared *via* photo-polymerization with UV irradiation for 8 min at 0°C.[13] In this study, capillary monolith columns of UV-polymerized poly(BMA-*co*-EDMA) were prepared at 0°C with various polymerization periods of 4, 8, 12, and 16 min, and the relationship between monomer conversion and the polymerization period was elucidated. About 10 mm of each column and the IS were subjected to Py-GC measurements and the conversions of BMA and EDMA were determined. With a polymerization period of 4 min, the average

conversions (n = 3) of BMA and EDMA were 23.8 and 43.2%, respectively (Fig. 3). The monomer conversions increased with increased polymerization periods and reached about 41.6% for BMA and 65.3% for EMDA with 16 min of polymerization. The greater conversion of EDMA compared to BMA indicates that the polymerization of EDMA proceeds at a faster rate under these polymerization conditions. A similar phenomenon was also reported for a thermally polymerized poly(BMA-*co*-EDMA) monolith.[6]   Therefore, the bifunctional EDMA monomer polymerizes faster than the monofunctional BMA monomer.

Conclusions

Monomer conversions to poly(BMA-*co*-EDMA) monolith fixed in a capillary column were assessed *via* Py-GC without any sample pretreatment. The proposed method will be applicable for other types of polymer monolith columns.   In the low-conversion poly(BMA-*co*-EDMA) monolith, the monomer composition did not match that of the reaction solution introduced into the capillary. A measurement of the actual monomer conversion is essential for further progress in improving polymer monolith columns. Studies of the correlation between the monomer conversion to polymer monoliths and various column properties are currently underway.

References

1. A. Ghanem and T. Ikegami, *J. Sep. Sci.*, **2011**, *34*, 1945.
2. F. Svec, *J. Chromatogr., A*, **2010**, *1217*, 902.
3. F. Svec, *J. Chromatogr., A*, **2012**, *1228*, 250.
4. L. Trojer, C. P. Bisjak, W. Wieder, and G. K. Bonn, *J. Chromatogr., A*, **2009**, *1216*, 6303.
5. A. Greiderer, L. Trojer, C. W. Huck, and G. K. Bonn, *J. Chromatogr., A*, **2009**, *1216*, 7747.
6. I. Nischang and O. Brüggemann, *J. Chromatogr., A*, **2010**, *1217*, 5389.
7. I. Nischang, I. Teasdale, and O. Brüggemann, *J. Chromatogr., A*, **2010**, *1217*, 7514.
8. M. Takahashi, T. Hirano, S. Kitagawa, and H. Ohtani, *J. Chromatogr., A*, **2012**, *1232*, 123.
9. T. P. Wampler (ed.), "*Applied Pyrolysis Handbook*", 2nd ed., **2006**, CRC Press, Boca Raton.
10. S. Tsuge, H. Ohtani, and C. Watanabe, "*Pyrolysis-GC/MS Data Book of Synthetic Polymers—Pyrograms, Thermograms and MS of Pyrolyzates—*", **2011**, Elsevier, Amsterdam.
11. E. F. Hilder, F. Svec, and J. M. Fréchet, *Electrophoresis*, **2002**, *23*, 3934.
12. H. Ohtani, T. Asai, and S. Tsuge, *Macromolecules*, **1985**, *18*, 1148.
13. T. Hirano, S. Kitagawa, and H. Ohtani, *Anal. Sci.*, **2009**, *25*, 1107.