Polymer Journal, Vol. 36, No. 3, pp. 205—208 (2004)

Trial Production and Evaluation of Gel Permeation Chromatograph Equipped with On-line Distiller for Mobile Phase Recycling

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(Received September 17, 2003; Accepted December 29, 2003)

ABSTRACT: In order to make a contribution to the economy of solvent and preservation of environment, a mobile phase on-line recycling system with distillation device of solvent was made on trial and incorporated to the conventional apparatus for gel permeation chromatography (GPC). Performance of the on-line recycling system was evaluated by the chromatograms obtained from the measurements of several standard monodisperse polystyrenes. As a result, the reproducibility and accuracy of the chromatograms obtained from the new type of GPC apparatus with mobile phase on-line recycling system were ensured. In addition, the safety of the mobile phase on-line recycling system was also proved to be reliable on the evidence of no existence of peroxide produced from THF.

KEY WORDS Gel Permeation Chromatograph / Mobile Phase / On-line Recycling / Distillation / Tetrahydrofuran / Economy of Solvent / Preservation of Environment /

Gel permeation chromatography (GPC), which is a kind of high performance liquid chromatography, has been widely used to evaluate the molecular weight (MW) and molecular weight distribution (MWD) of polymer since Moore revealed the use of a kind of polystyrene gel synthesized from styrene and divinylbenzene for separating synthetic polymers soluble in organic solvents in 1964.[1]

As usual, one-way system of mobile phase is used in the conventional GPC apparatus, including solvent reservoir, pump, sample injector, chromatographic column, detector, solvent receiver, and so on.[2] This means large-scale of solvent should be used, and as a result, it leads up to large-scale of waste solvent. So that it costs too much on the treatment of waste solvent, and at the same time, environmental problem resulted from the waste solvent is also feared.

In this study, for the purpose of making a contribution to the economy of solvent and preservation of environment, a new type of GPC apparatus with a mobile phase on-line recycling system was made on trial and run on test for over four years by using tetrahydrofuran (THF) as mobile phase. Several standard monodisperse polystyrenes were used for measuring samples to obtain the chromatograms from the new type of GPC apparatus and the conventional one, respectively. The properties of reproducibility and accuracy on the chromatograms obtained from the new type of GPC apparatus with mobile phase on-line recycling system were evaluated. Furthermore, the running safety of the mobile phase on-line recycling system was also investigated.

EXPERIMENTAL

Materials

Five kinds of standard monodisperse polystyrenes used in this study were purchased from Senshu Scientific Co., Ltd., with the MW of 67500, 32500, 9100, 3420, and 1600, respectively. THF containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 300 ppm) as an antioxidant was supplied by Kanto Chemical Co., Inc. and used as the mobile phase in this study.

GPC Apparatus

Figure 1 shows schematic diagram of the conventional GPC apparatus, which was composed of solvent

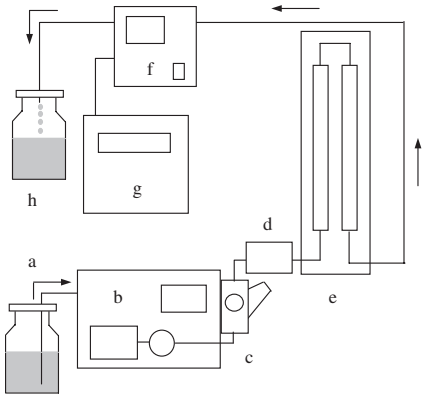

Figure 1. Schematic diagram of the conventional GPC apparatus. a, solvent reservoir; b, pump; c, sample injector; d, guard column; e, separation columns; f, detector; g, integrator; h, solvent receiver.

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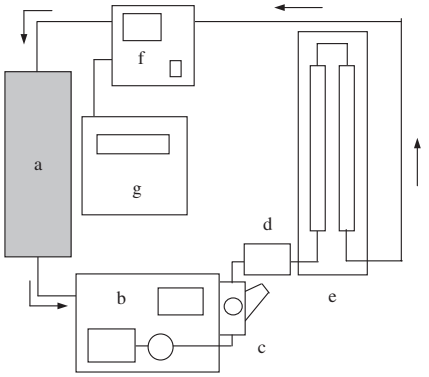

Figure 2. Schematic diagram of the new GPC apparatus with mobile phase recycling system. a, solvent recycler; b, pump; c, sample injector; d, guard column; e, separation columns; f, detector; g, integrator.

reservoir, pump, sample injector, guard column, separation columns, detector, integrator, and solvent receiver. The new type of GPC apparatus with the mobile phase on-line recycling system was made on an experimental basis and the schematic diagram is shown in Figure 2. Comparing with the conventional apparatus, the on-line recycling system used a distillation device of mobile phase instead of the solvent reservoir and solvent receiver. The detailed device of mobile phase recycler is shown in Figure 3.

The distillation part is described by the route with solid arrows, composed of solvent reservoir (c, volume: 1000 mL), GPC (d), distiller (i), and fan cooler (e) in turn. The distiller was a pressure-resistant Pyrex test tube (inside diameter: 20 mm, length: 400 mm, pressure limit: 5 MPa), which was coiled a nichrome wire (g) as heater. Waste solvent flowed into the distiller was recycled in situ and the height of the stored solvent was about 100 mm from bottom. The heating temperature was set at 87 °C, which is about 20 °C higher than the boiling temperature of THF. And the heater was controlled by thermocouple (h) and temperature controller (j). Usually, the total volume of solvent used in the reservoir was about 600–700 mL and the feeder syringe (f) was used to replenish with the solvent in the reservoir when it was less than 100 mL. The waste-out syringe (k) was used to drain the waste liquid including THF and polymer from the distiller about every 3 months when the test tube needed to be cleaned.

On the other hand, a security part was also made on trial because THF is a kind of ethers which are easy to be oxidized in air and the oxidation product named as peroxide is very dangerous during the distillation.[3,4] To be concrete, the security part is described by the route with dashed arrows, composed of nitrogen cylinder (l), distiller (i), fan cooler (e), solvent reservoir (c), deodorizing trap (active carbon, b), and deodorizing trap (water, a) in turn. Before and after the running of distiller, nitrogen purging (50 mL min^{-1}) was carried out to eliminate oxygen from the distillation system completely and prevent a reversed flow of air.

Furthermore, because the boiling temperature of BHT is 265 °C, which is higher than the distillation temperature, it would be left in the distiller after distillation. As a result, the BHT in the solvent reservoir will be decreasing on the cycling times of THF. So that, before the nitrogen purging, about 1 mL THF was taken a sample from the solvent reservoir and the coloration reaction between the sample and potassium iodide was carried out to confirm whether the peroxide was existed or not.[5]

Measurements

Test conditions of GPC apparatus are listed in Table I. Standard monodisperse polystyrenes were

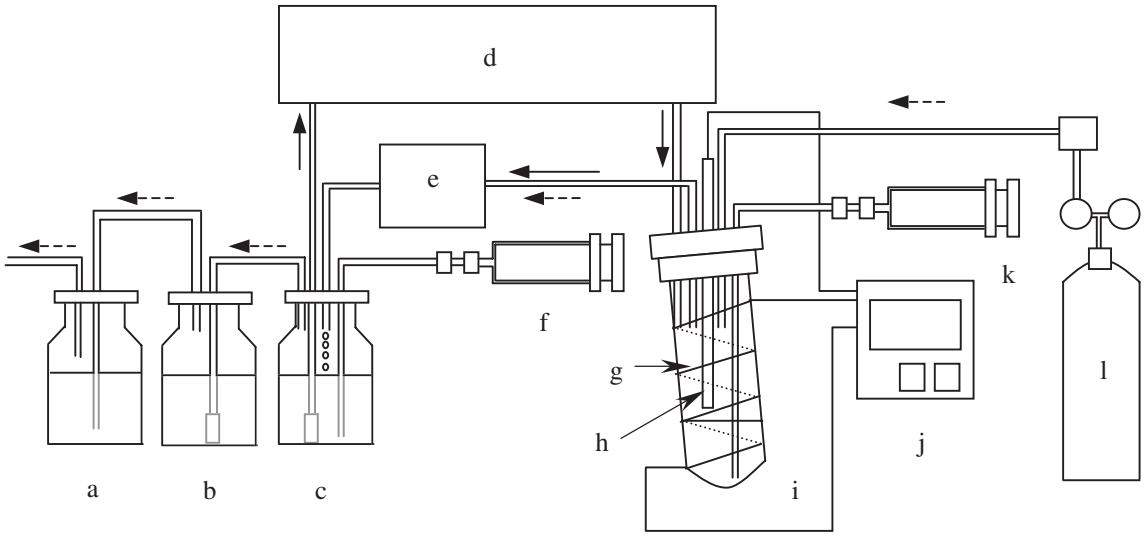

Figure 3. Device of mobile phase recycling system. a, deodorizing (water); b, deodorizing (active carbon); c, solvent reservoir; d, GPC; e, fan cooler; f, feeder syringe; g, heater; h, thermocouple; i, distiller; j, temperature controller; k, waste-out syringe; l, nitrogen cylinder.

Table I. Test conditions

Sample:	500 μL PS mixture (0.1 w/v%)
Column:	Shodex KF-804-L→KF-803-L
Column temp.:	45 °C
Mobile phase:	THF
Pump:	Hitachi L-6000
Flow rate:	1.0 mL min^{-1}
Detector:	Shimamura RI (YRD-880 midget)
Integrator:	Hitachi D-2520
Chart speed:	10 mm min^{-1}

measured by the one-way system GPC and the on-line recycling system GPC, respectively. THF in the reservoir was used as the dissolving solvent of polystyrenes. Influence of the cycle times of THF on the reproducibility of chromatogram was investigated. Moreover, the accuracy of the chromatogram obtained from the on-line recycling system GPC was also evaluated by comparing it with the result obtained from the one-way system. Consumption of THF during the period of running test was calculated on the basis of measuring times, and the economical characteristic of the recycling system was discussed.

RESULTS AND DISCUSSION

Reproducibility of Chromatogram

Figure 4 shows the reproducibility of chromatograms measured by the GPC apparatus with mobile phase on-line recycling system. Two kinds of standard monodisperse polystyrenes, with the MW of 32500 (a) and 3420 (b), were used as the samples. The codes of (A), (B), (C), and (D) mean the chromatograms obtained after 2, 5, 10, and 20 cycles of THF, respectively. The cycles of THF were determined from the total volume of THF in the solvent reservoir divided by the flow rate of THF.

From the results of chromatograms, it can be found that the peaks of the samples nearly have no changes on the shape and the position, even if the cycling times of THF was extended to 20 times. It can also be seen that the mobile phase on-line recycling system has no influence on the flat of the baseline. So that the reproducibility of chromatogram obtained from the GPC apparatus with mobile phase on-line recycling system was proved to be reliable.

Accuracy of Chromatogram

Figure 5 shows the chromatograms of three kinds of standard monodisperse polystyrenes measured by the on-line recycling (A) and one-way (B) system GPC apparatus, respectively. Molecular weights of the three kinds of polystyrenes were 67500 (a), 9100 (b), and 1600 (c).

It can be seen that the peak values of the standard

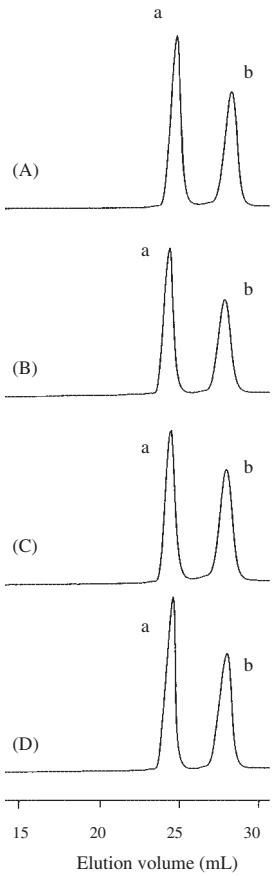

Figure 4. Chromatograms of monodisperse polystyrenes measured by the GPC apparatus with mobile phase recycling system. (A), after 2 cycles of mobile phase; (B), after 5 cycles of mobile phase; (C), after 10 cycles of mobile phase; (D), after 20 cycles of mobile phase. MW: 32500 (a); 3420 (b).

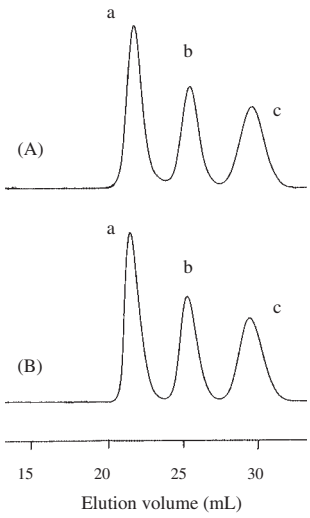

Figure 5. Chromatograms of monodisperse polystyrenes. (A), measured by the GPC apparatus with mobile phase recycling system after 20 cycles of mobile phase; (B), measured by the conventional GPC apparatus. MW: 67500 (a); 9100 (b); 1600 (c).

monodisperse polystyrenes (a, b, and c) in the chromatogram, which was obtained from the GPC apparatus with on-line recycling system, quite correspond to

Table II. Results of running test

Period of date:	1999.3.5–2003.6.18
Days:	839 days
Measuring times:	3849 times
Consumption of THF:	26.55 L (recycling system)
	115.47 L (one-way system)

those from one-way system GPC apparatus, although the chromatogram was obtained after 20 cycles of THF. Moreover, the flat of baseline and the sensitivity of detection were so good as the results obtained from the one-way system GPC apparatus. So that the accuracy of the chromatogram obtained from the new type GPC apparatus with mobile phase on-line recycling system was proved to be reliable for evaluating MW of polymer.

Consumption of THF

Table II shows the comparing results about consumption of THF between the one-way system GPC apparatus and the on-line recycling system GPC apparatus. The period of running test was over four years, with 839 test days and 3849 test times.

It was understood that the consumption of THF was about 26.55 L by using the on-line recycling system GPC apparatus. On the other hand, if the one-way system GPC apparatus were used, the consumption of THF would increase to about 115.47 L. As a result, comparing with the one-way system, total consumption of the mobile phase was too much little by using the on-line recycling system. And because the waste solvent resulted from the measurement was recycled by the distiller simultaneously, the treatment of waste solvent was also efficient and convenient.

Confirmation of Safety

During the passed four years of running test, it was confirmed that there was no peroxide of THF produced if the nitrogen purging was exactly carried out before and after the running of distillation. But when the apparatus was not used for more than one week, for example, in the winter or summer holiday, the peroxide was checked out sometimes although it was not too much, so that the liquids in the reservoir and distiller should be renewed before running. As a result, the safety of the new GPC apparatus with mobile phase on-line recycling system can also be thought to be reliable.

CONCLUSIONS

To be summarized, the reproducibility and accuracy on evaluating the MW and MWD of polymer were confirmed to be reliable by using the new type apparatus of GPC with on-line recycling system of mobile phase. Moreover, comparing with the conventional GPC apparatus, the new GPC apparatus with mobile phase on-line recycling system was proved to be useful for its excellent economy of solvent. And because the waste solvent can be reduced drastically, the mobile phase on-line recycling system can also make a great contribution to the environmental protection. In addition, with strict system to purge oxygen from the solvent by inert gas, the new type of GPC apparatus with mobile phase on-line recycling system is very safe and can be applied to the oxidizable solvent, such as THF and so on.

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