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Size-exclusion chromatography on polyhydroxymethacrylate gel with dimethylformamide as eluent

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Abstract

Size-exclusion chromatography (SEC) in dimethylformamide (DMF) on polyhydroxymethacrylate (PHMA) gel has been compared with SEC on polystyrene–divinylbenzene (PS–DVB) gel. Comparison of the molecular mass calibration curves on the two gels at similar size-exclusion limits shows that the calibration curves on PHMA, particularly for low size-exclusion limits ($<2 \cdot 10^5$), have wider effective molecular mass ranges than those on PS–DVB. This leads to better separation of low-molecular-mass polymer peaks from system peaks on PHMA and also better resolution of oligomer peaks. Hydrophobic polymers, such as polystyrene standards and polydimethylaminostyrene, were not eluted by size-exclusion chromatography on PS–DVB due to hydrophobic interaction: they were, though, eluted satisfactorily on PHMA.

1. Introduction

Recently, an increasing number of high-performance polymers has been emerging, which derive their exceptional properties from specific functional groups in their structures. These polymers tend to be soluble in polar organic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP) and hexafluoroisopropanol (HFIP), and to have ionic properties in solution. The molecular mass distributions of these polymers are often measured by size-exclusion chromatography (SEC). Such polar organic solvents, in particular DMF, are often used as eluents, with a small amount of salt added, in combination with columns of polystyrene–divinylbenzene (PS–DVB) gel, porous glass, silica gel, cellulose gel, etc., the most popular packing being PS–DVB gel [1–10].

A major problem in SEC with DMF as the eluent are the nonexclusion effects that arise from substrate–polymer interactions [2]. When a PS–DVB gel was used as a packing material and polystyrene standards were eluted, the elution volumes were far greater in DMF than in tetrahydrofuran (THF), which was due to the adsorption of the polymer on the substrate in DMF. Such adsorption could be eliminated by using a nontreated glass as the packing material in DMF, but then polymers with strong hydrogen-bonding functionalities adsorbed markedly on the substrate.

Another problem we have experienced with the use of DMF as an eluent with PS–DVB-gel-packed columns is a narrow effective molecular-mass range of the calibration curve when a column with a small size-exclusion limit (molecu-

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lar mass ≤20 000) is used alone or in series with a column with a larger size-exclusion limit. This may be due to DMF not being sufficiently compatible in polarity with the PS–DVB gel. PS–DVB is very hydrophobic and is not completely wetted by DMF, a rather polar solvent. Therefore, small PS–DVB pores are not sufficiently swollen by DMF and are not sufficiently accessible to analyte polymers.

This study represents an attempt to solve these problems. Polyhydroxymethacrylate (PHMA) gel was used as the packing material for SEC in DMF as an alternative to PS–DVB or silica gel. A comparison is made between PHMA and PS–DVB as regards the calibration curves and separations of various polymers.

2. Experimental

The liquid chromatograph employed was a Shodex GPC System-21 (Showa Denko, Tokyo, Japan) consisting of a solvent delivery pump, a sample injector and a refractive index (RI) detector, all enclosed in a housing thermostatted at 35°C, the separation columns being held in a separate column oven. Measurements were made by processing the signals from the detector in a SIC Labchart180 integrator. Since the whole system was thermally equilibrated, the deviation coefficients of the standard-sample elution volumes were within 0.05%.

The PHMA-gel-packed columns were Shodex OHpak SB-800 HQ series, 300 × 8.0 mm I.D. Since aqueous solutions are usually used as eluents for the SB-800 HQ series, aqueous solutions in the columns were first replaced by DMF by delivering DMF at 0.3 ml/min for 2–3 h. The PS–DVB-gel-packed columns to be compared were Shodex GPC KD-800 series, also 300 × 8.0 mm I.D. These columns are used solely in combination with DMF.

The PS standards used for calibration were Shodex Standard S series with M_p (peak top molecular mass) ranging from 580 to 7 104 000. The PEO standards were PEO-7 and PEG-10 series with M_p ranging from 106 to 1 400 000 (Polymer Laboratories, Shropshire, UK). A solution containing three or four standards with M_ps sufficiently different to permit separation was injected each time. For each data point three measurements were averaged. DMF and lithium bromide were of the purest grade from Wako (Tokyo, Japan), and used as obtained. The polymers analyzed by SEC were polycarbonate, phenol–formaldehyde resols and polydimethylaminostyrene. Polycarbonate (mass-average molecular mass $M_w = 28\,800$) was purchased from General Science Corporation (Tokyo, Japan); the phenol–formaldehyde resols were a gift from Showa Kobunshi (Takasaki, Japan) and polydimethylaminostyrene was a gift from Nippon Paint (Osaka, Japan).

3. Results and discussion

3.1. Calibration curves

Fig. 1 shows the calibration curves in DMF for the Shodex OHpak SB-800 HQ series based on the PS standards and Fig. 2 shows the calibration curves for the Shodex GPC KD-800 series based on the PEO standards. In terms of size-exclusion limit, SB-802.5 HQ (exclusion limit 10^4) corresponds to KD-802.5 (size exclusion limit $2 \cdot 10^4$), SB-803 HQ ($2 \cdot 10^5$) to KD-803 ($7 \cdot 10^4$), SB-804 HQ (10^6) to KD-804 ($4 \cdot 10^5$), SB-805 HQ ($4 \cdot 10^6$) to KD-805 ($4 \cdot 10^6$) and SB-806 HQ ($2 \cdot 10^7$) to KD-806 ($2 \cdot 10^7$). Comparison of the calibration curves for the corresponding columns of the two series shows that the calibration curves for the SB-800 HQ series, particularly at the lower size-exclusion limits ($<2 \cdot 10^5$), are wider in their effective molecular mass ranges. As a typical example, a comparison of the calibration curves for SB-802.5 HQ and KD-802.5 is shown in Fig. 3. The effective molecular mass range of the calibration curve for SB-802.5 HQ is roughly from 10^4 to less than 100, while that for KD-802.5 is from 10^4 to $3 \cdot 10^2$. Therefore, the former is about four times wider than the latter.

The reason for this difference may be the degree of matching in polarity between the eluent and the gel. The PHMA gel matches DMF in polarity and is better wetted by DMF

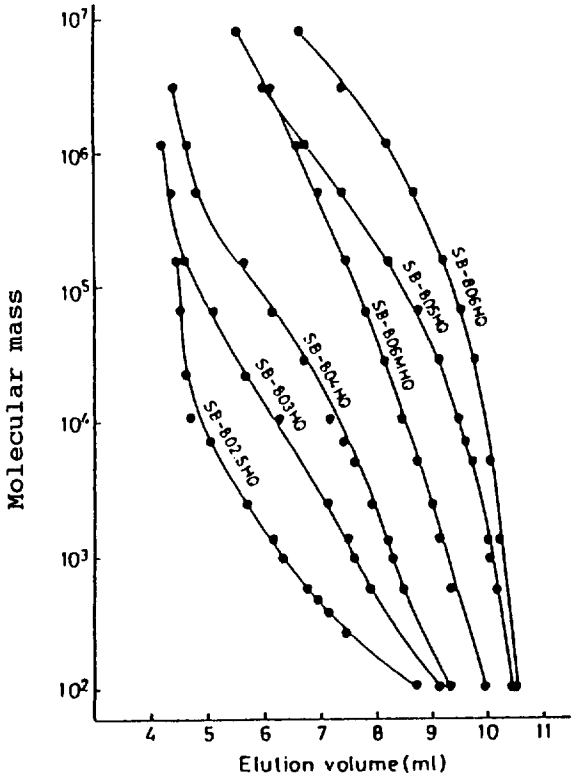

Fig. 1. Calibration curves for Shodex OHpak SB-800 HQ series. PS standards; column temperature, 40°C; eluent, DMF + 5 m*M* LiBr; flow-rate, 1.0 ml/min; RI detector.

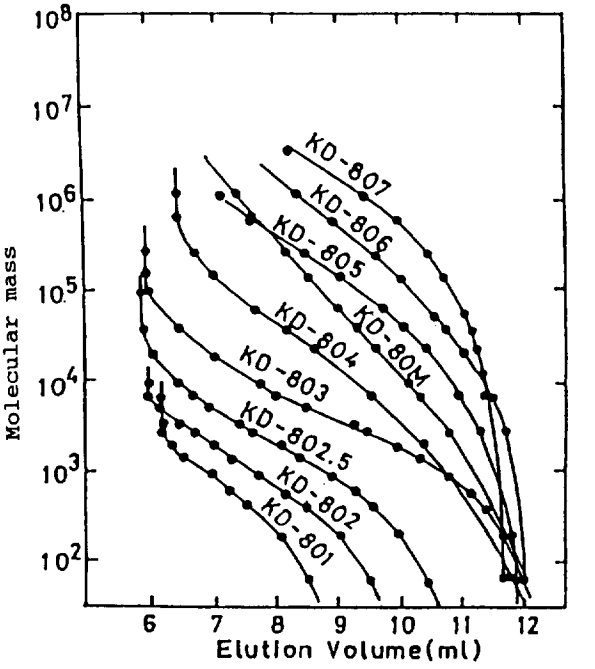

Fig. 2. Calibration curves for Shodex GPC KD-800 series. PEO standards; column temperature, 40°C; eluent, DMF + 5 m*M* LiBr; flow-rate, 1.0 ml/min; RI detector.

than the far less polar PS–DVB gel. Small PHMA pores thus swell more easily and can be made more accessible to analyte polymers in DMF. The dotted line represents the calibration curve for KD-802.5 in THF based on the PS standards. The effective molecular mass range is almost equal to that observed for SB-802.5 in DMF. Here, too, the matching in polarity between PS–DVB and THF would appear to provide the explanation.

Comparison of the calibration curves based on PS and PEO standards respectively for SB-802.5 and KD-802.5 shows that the calibration curve based on the PS standards almost coincides with that based on the PEO standards for SB-802.5, but that the former deviates from the latter in the higher elution volume direction for KD-802.5, indicating adsorption of the PS standards on the PS–DVB gel [2], which is attributed to

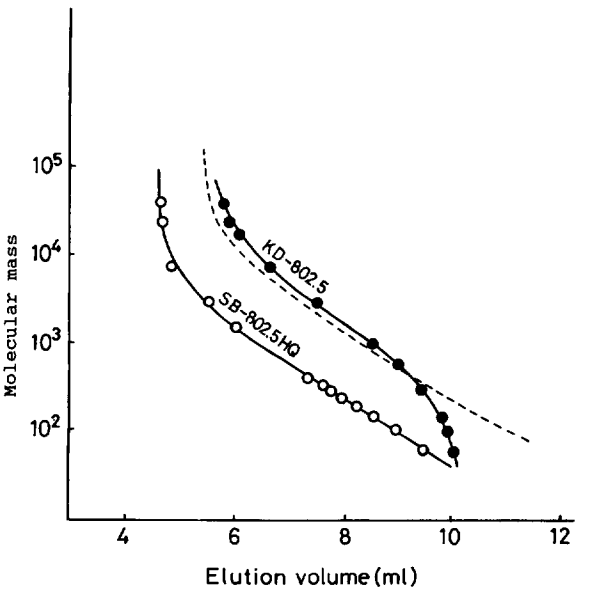

Fig. 3. Comparison of the calibration curves on SB-802.5 HQ and KD-802.5. PEO standards; column temperature, 40°C; eluent, DMF + 5 m*M* LiBr; flow-rate, 1.0 ml/min; RI detector. The dotted line represents the calibration curve in THF on KD-802.5 based on the PS standards.

hydrophobic interaction. It is understood that no hydrophobic interaction exists between the PS standards and the PHMA gel.

3.2. Separations of various polymers

Fig. 4 shows the chromatograms of phenol–formaldehyde (PF) resols separated, respectively, on a column set comprising SB-802.5 HQ + SB-804 HQ (PHMA-gel-packed columns) and a set comprising KD-802.5 + KD-804 (PS–DVB-gel-packed columns), with DMF plus 5 m*M* lithium bromide as the eluent in both cases. It is apparent that the PHMA-gel-packed column system gives better results, oligomers being better separated from each other and from system peaks. In addition, judging from the shapes of the chromatograms obtained on the two systems, a further drawback of PS–DVB-gel-packed columns would seem to be that high-molecular-mass

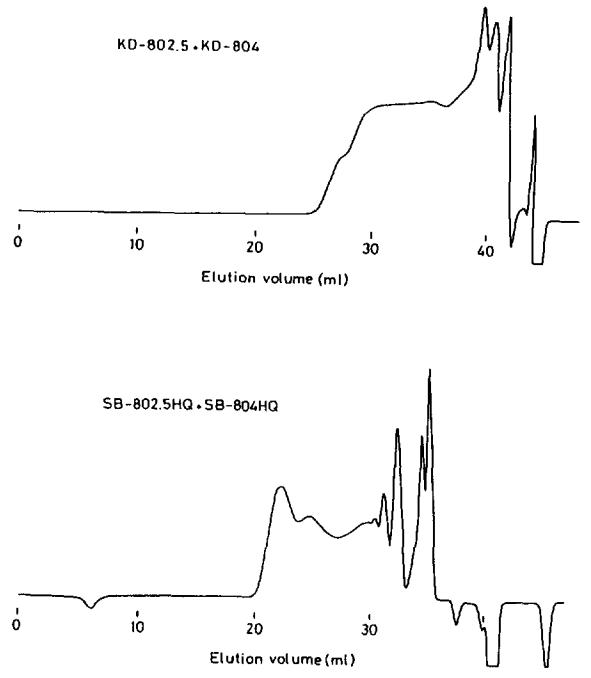

Fig. 4. Chromatogram of PF resols separated respectively on the column sets SB-802.5 HQ + SB-804 HQ and KD-802.5 + KD-804. Eluent, DMF + 5 m*M* LiBr; flow-rate, 0.5 ml/min; column temperature, 40°C; RI detector; sample concentration, 0.5%; injection volume, 100 μl.

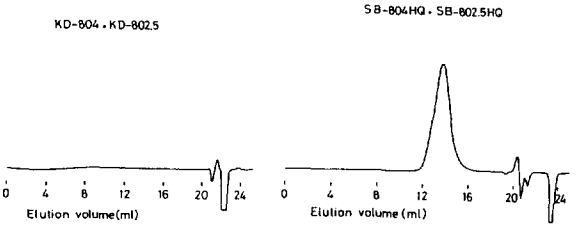

Fig. 5. Chromatograms of polydimethylaminostyrene separated on SB-802.5 HQ + SB-804 HQ and on KD-802.5 + KD-804. Flow-rate, 1.0 ml/min. All other conditions as for Fig. 4.

constituents are retained on the columns by reversed-phase chromatography.

Polydimethylaminostyrene is a recently developed high-performance polymer which possesses an amino group in its structure and behaves as a base in DMF. For the determination of its molecular mass, both SB-802.5 HQ + SB-804 HQ and KD-802.5 + KD-804 were used in combination with DMF plus 5 m*M* lithium bromide as the eluent. It was found that the polymer was retained and not eluted at all on KD-802.5 + KD-804, while it was eluted as a normal Gaussian peak on SB-802.5 + SB-804, as shown in Fig. 5. The reason may again be hydrophobic interaction with the PS–DVB gel and the absence of such an interaction with the PHMA gel.

In the SEC of this basic polymer, addition of triethylamine to the eluent (DMF + 5 m*M* lithium bromide) affected the molecular mass measurement. The results are shown in Table 1. The molecular mass averages determined following addition of 0.2% triethylamine to the eluent are somewhat larger than those obtained without

Table 1
Effect of addition of triethylamine (TEA) to the eluent on molecular-mass measurement

TEA (%)	Peak top (min)	M_n	M_w	M_w/M_n
0.2	13.70	$8.87 \cdot 10^3$	$1.38 \cdot 10^4$	1.56
0.0	13.47	$1.02 \cdot 10^4$	$1.68 \cdot 10^4$	1.64

Conditions: column set, SB-802.5 + SB-804; flow-rate, 1.0 ml/min; sample concentration, 0.5%; eluent, DMF + 5 m*M* LiBr; column temperature, 40°C; injection volume, 100 μl.

this addition. It is inferred that the ionized polymer is retained on the gel in DMF not only by size-exclusion, but also by ionic interaction with a trace amount of carboxyl groups on the gel, ionization being suppressed by the addition of triethylamine.

An advantage of using PHMA gel is the wide usable pH range (2–10), which permits the addition of acids or bases to the eluent for suppression of the ionic interactions. When a silica packing is used, hydrophobic interactions may be minimal, but addition of bases to the eluent is precluded.

Fig. 6 shows the chromatograms of polycarbonate obtained on SB-802.5 HQ + SB-805 HQ and KD-802.5 + KD-805 using DMF + 5 m*M* lithium bromide as eluent. The biggest difference between the two chromatograms is the better separation of the polymer peak from the system peak on SB-802.5 HQ + SB-805 HQ. Since the polymer peak can also be defined more precisely from beginning to end, the use of the SB-800 HQ series should therefore lead to more precise determination of molecular mass averages.

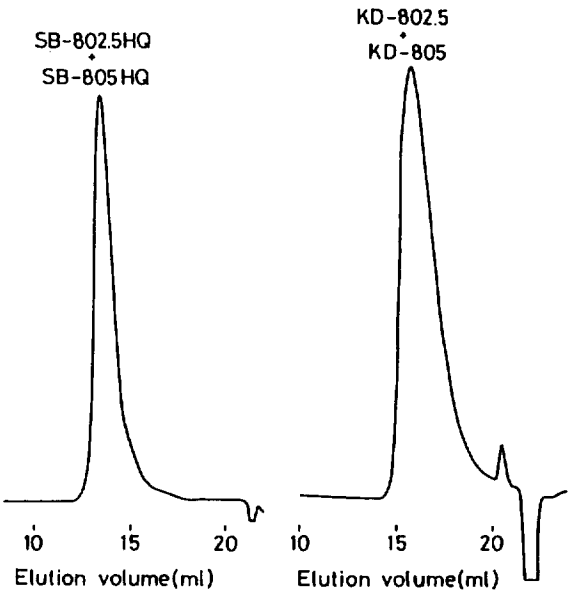

Fig. 6. Chromatograms of polycarbonate separated on SB-802.5 HQ + SB-805 HQ and on KD-802.5 + KD-805. Conditions as for Fig. 5.

4. Conclusion

PHMA gel has been evaluated as a packing material for size-exclusion chromatography when DMF is used as the eluent. It was found that, with this eluent, PHMA gel has advantages over PS–DVB gel and silica: nonexclusion effects, including hydrophobic interaction and ionic interaction, can be eliminated; and, even with columns with low size-exclusion limits, it provides a wide effective molecular mass range.

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