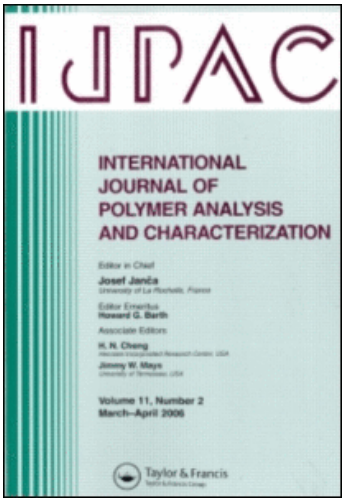

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Evaluation of "Solvent-Peak Separation" Column for the Determination of Polymer Molecular Mass Averages by SEC

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The poor baseline recovery between the end of the polymer chromatogram and the beginning of the solvent-related impurity peaks is often encountered in size exclusion chromatography. Also oligomers included in the polymer samples disturb the baseline recovery. The arbitrary selection of the end of the polymer chromatogram for the calculation of molecular mass averages is one of the most restrictive aspects of accurate measurement of the number-average molecular mass; inclusion of low-molecular mass materials results in underestimation of number-average molecular mass. The connection of a short-column packed with packing materials of a small pore size was shown to effectively separate the polymer chromatogram from the solvent-related impurity peaks and to allow the proper selection of the baseline.

Keywords: Size exclusion chromatography, number-average molecular mass, baseline, cutoff, molecular mass

INTRODUCTION

Size exclusion chromatography (SEC) measures both weight-average (M_w) and number-average (M_n) molecular masses (MM) of polymers at the same time. In order to calculate MM averages from the SEC chromatogram of a

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polymer, one has to draw a linear baseline between the beginning and end of the polymer chromatogram. The zero signal of the detector of the SEC system, defined as a baseline, is taken as a straight line in the zone between the sample injection point and the exclusion limit of the column system and in the zone after the last impurity peak. No elution will take place in these zones in an ideal SEC separation and the intrapolation of the baseline from the former zone to that of the latter zone superimposes the baseline of the polymer chromatogram.

The establishment of the beginning of the polymer chromatogram is rather straightforward and that of the end of the polymer chromatogram can be difficult. When baseline resolution between the polymer chromatogram and the solvent-related impurity peaks, such as antioxidants and oxidized antioxidants (henthforce referred to as the solvent peaks), is attained, that is, the polymer chromatogram is separated completely from the solvent peaks, then the choice of the end of the polymer chromatogram is obvious. However, when the polymer chromatogram is incompletely separated from the solvent peaks and the baseline separation is not attained, the establishment of the correct baseline is questionable.

The poor baseline recovery after the polymer chromatogram is often encountered. This is a serious problem in establishing the correct baseline and the end-point limit for the chromatogram, which results in poor reproducibility of M_n values.[1–3] Oligomers included in the polymers may disturb baseline recovery.[4] In some instances, the detector response from the oligomeric materials of the polymers may coincide with the onset of the response for the solvent peaks.

The purpose of this investigation is concerned with improving the baseline recovery. One of the possible ways is to draw the response of the low-MM portion (mainly oligomers) in the polymer apart from the solvent peaks. For this purpose the addition of an SEC column packed with a small-pore size packing materials can be considered. The evaluation of a "Solvent-Peak Separation" column exclusively designed for this purpose is discussed.

EXPERIMENTAL

SEC measurements were performed on a Jasco TRIROTAR high-performance liquid chromatograph (Jasco Corp., Tokyo, Japan) with a model SE-31 differential refractometer (RI) and a model KT-15 solvent degasser (both from

Showa Denko K. K., Tokyo, Japan). Two SEC column systems were used in this study: column system A consisted of two Shodex SEC KF 806L (300-mm × 8-mmi.d.) columns (Showa Denko) which are used for polymer separation and are packed with a mixture of polystyrene (PS) gels of different exclusion limits (the estimated maximum exclusion limit of the column is 2×10^7 MM as PS). Column system B is two Shodex SEC KF 806L columns and one Shodex SEC KF 800D (100-mm × 8-mmi.d.) column (commercial name "Solvent-Peak Separation" column) packed with PS gel of small-pore size (comparable to PS gel packed in a Shodex SEC KF 801 column which has an exclusion limit of PS MM of 1,000). The short column was connected after the polymer separation columns.

Samples used in this experiment were SRM 706 PS (NIST, Washington, DC), reprecipitated SRM 706 PS, and two commercial PS samples (designated as PS-1 and PS-2). The reprecipitation of SRM 706 PS was performed to remove low MM materials and the procedure was as follows: 1g of polymer was dissolved in 100 mL chloroform and the solution was poured into 500 mL of methanol dropwise, followed by filtration of the precipitate and by drying the precipitate to constant weight at 40 °C under reduced pressure for 24 h.

The calibration curves of the SEC systems were constructed by determining the peak retention volumes of PS standards of narrow MM distributions. PS standards were purchased from Tosoh Company (Tokyo, Japan).

Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min. The sample concentrations were 0.12% for PS samples and 0.02 to 0.04% for PS standards. The injection volume of the sample solutions was 0.25 mL. The attenuation of the RI detector was ×8.

RESULTS AND DISCUSSION

Calibration curves of column systems A and B are shown in Figure 1. The calibration curve of column system B shifted 1.6 mL to the right of that of column system A and the slopes of the two calibration curves are the same down to MM 2,000 from the higher MM region.

Chromatograms of SRM 706 PS measured with both column systems are shown in Figure 2. The chromatograms were recorded on a strip chart recorder. The intrapolation of the baseline at the injection point of the sample solution to the beginning of the polymer chromatogram to the

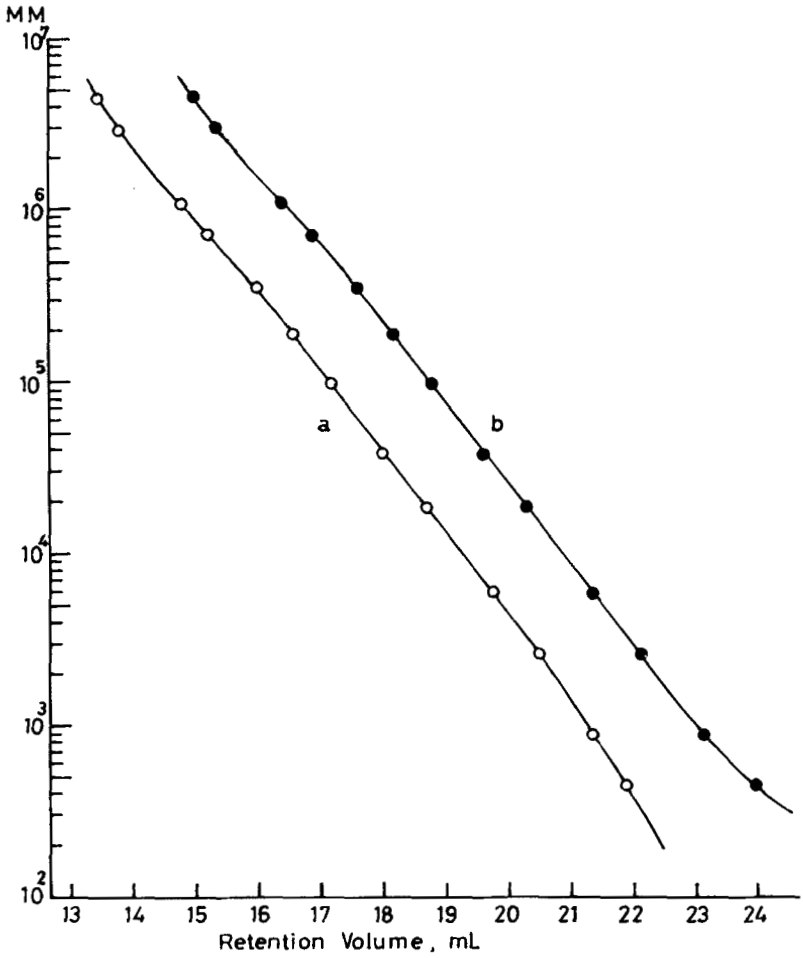

FIGURE 1 Calibration curves of (a) column system A and (b) column system B.

end of the solvent peaks agreed well with the baseline drawn between the beginning of the polymer chromatogram and the end of the solvent peaks (*see* Fig. 2 (a)). In chromatogram (a) (SRM 706 PS obtained with column system A), the detector signal after retention volume (V_R) 21.4 mL ($MM = 850$) was flat and parallel with the baseline. This flat response was verified to be due to the elution of low MM materials such as oligomers below MM 1,000.[4]

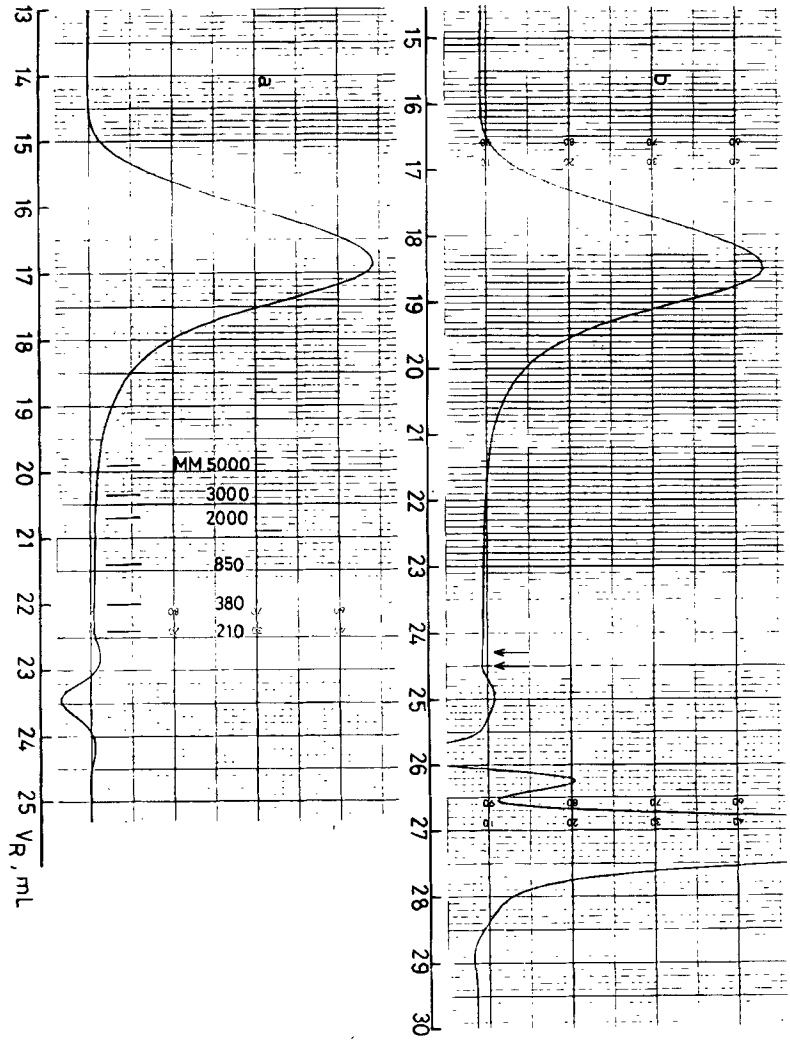

FIGURE 2 Chromatograms of SRM 706 PS obtained with (a) column system A and (b) column system B.

In column system A, the retention volume of the beginning of the solvent peaks in Figure 2(a) was 22.4 mL and MM was 210 from Figure 1(a). Similarly MM at V_R 21.4 mL was 850. The arbitrary selection of the evaluation of the polymer chromatogram limit is one of the most restrictive

aspects for accurate MM average measurements by SEC. The assignment of the low-MM limit intuitively may cause the dominant error for the value of M_n.[5] According to the DIN standard procedure, the monomer peak at the low MM end shall be included in the evaluation and if the monomer peak is eluted in the solvent peak area, or if the end of the polymer chromatogram extends into the area of solvent peaks, the chromatogram cannot be evaluated for the caluculation of MM averages.[6]

Molecular mass averages calculated at different cutoff MM are listed in Table I. The values of M_n increased with increasing cutoff MM. Inclusion of the responses of low MM materials resulted in the extremely low values of M_n. The influence of cutoff MM to the values of M_w was almost negligible.

The certificated values of SRM 706 from NIST were 2.58×10^5 for M_w and 1.37×10^5 for M_n. The value of M_n by NIST was obtained by membrane osmometry and it is usually considered to be higher than the true value because of the permeation of polymer molecules less than MM 10^4 through the membrane used for the membrane osmometry experiment. However, the value of M_n which was obtained by inclusion of the all responses before the solvent peaks into the calculation of MM averages (V_R = 22.4 mL, MM = 210) was extremely low compared with that obtained by membrane osmometry, although the permeation of low-MM materials is considered in membrane osmometry. The question is how does one select the proper MM cutoff.[4]

The onset of the response for the solvent peaks to that of the low MM portion of the polymer chromatogram must also be considered. The connection of a "Solvent-Peak Separation" column to polymer separation columns (column system B) had the distinct effect of moving the polymer

TABLE I Molecular mass averages of SRM 706 PS at different cutoff molecular mass values

Column system A				*Column system B*			
V_R mL	*Cutoff MM*	M_w $\times 10^{-5}$	M_n $\times 10^{-4}$	V_R mL	*Cutoff MM*	M_w $\times 10^{-5}$	M_n $\times 10^{-4}$
19.9	5,000	2.48	9.53	21.5	5,000	2.49	10.5
20.35	3,000	2.47	8.82	21.95	3,000	2.49	10.0
20.7	2,000	2.47	7.94	22.3	2,000	2.49	7.53
21.4	850	2.47	6.71	23.0	1,000	2.49	7.19
22.0	380	2.45	4.68	23.5	650	2.48	7.04
22.4	210	2.45	3.82	24.3	360	2.48	5.65

chromatogram from the solvent peaks which makes it easier to select the proper baseline. The example is shown in Figure 2(b) for SRM 706 PS. The beginning of the solvent peak (the second arrow at V_R = 24.5 mL, MM = 320) is just after the end of the polymer chromatogram (the first arrow at V_R = 24.3 mL, MM = 360). The response of the vicinity near the end of the polymer chromatogram decreased evenly and was not parallel to the baseline. The difference of M_n by changing the cutoff MM in column system B was small compared to that in column system A (see Table I). The connection of a "Solvent-Peak Separation" column to polymer separation columns decreased the onset of the response of the solvent peaks to the response of low MM portion of the polymer chromatogram and made the calculation of M_n values more accurate.

As can be seen in Figure 1, the distance of the two calibration curves was 1.6 mL and the linear calibration plot for column system B was parallel to that for column system A down to MM 2,000 (the same slope). This means that no deformation of the calibration curve was observed over the entire range of the calibration curve except MM less than 2,000 and that the calculation of MM averages was not influenced by the connection of the "Solvent-Peak Separation" column. The calibration plot for column system B deviated from linearity below MM 2,000. The connection of such a short column can separate the polymer chromatogram from the solvent peaks without deforming the shape of the calibration curve, and allows the calculation of MM averages to be done much easier without changing the values of M_w.

Chromatograms of several PS samples obtained with column systems A and B are shown in Figures 3 to 5. Figure 3 shows the baseline separation between the polymer chromatogram and the solvent peaks. The end of the polymer chromatogram was V_R = 22.0 mL (MM = 380) for column system A and 24.0 mL and 430 for column system B. PS-1 sample has M_w 3.87×10^5 and M_n 1.34×10^5 obtained from a previous study [2]. Figure 4, although the baseline resolution was attained at V_R = 24.0 (MM = 430) in column system B (Fig. 4(b)), the solvent peaks in column system A overlapped the response of the low-MM portion of the polymer chromatogram and MM of the end of the polymer chromatogram was 250. PS-2 sample has M_w 1.61×10^5 and M_n 3.67×10^4. Figure 5 shows chromatograms of reprecipitated SRM 706 PS and the baseline separation was attained at V_R = 22.1 mL (MM = 330) even in column system A (Fig. 5(a)). The baseline separation in column system B was at V_R = 23.9 mL (MM = 470).

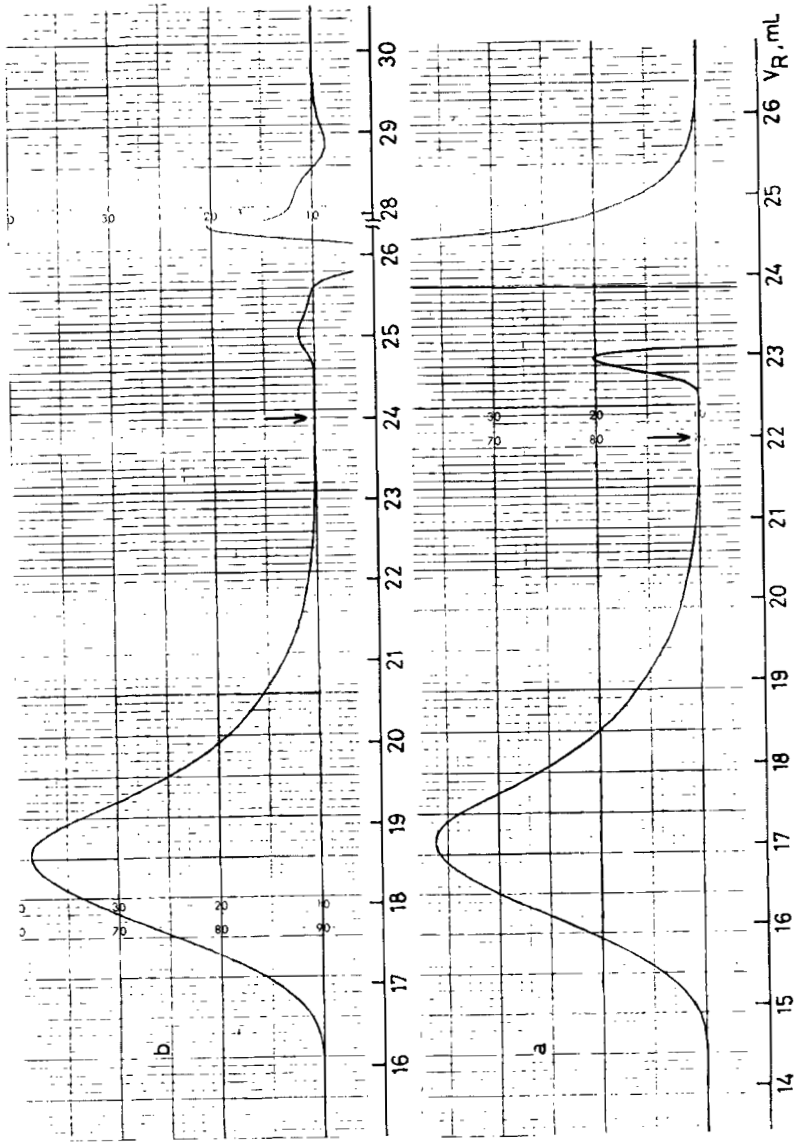

FIGURE 3 Chromatograms of PS-1 obtained with (a) column system A and (b) column system B.

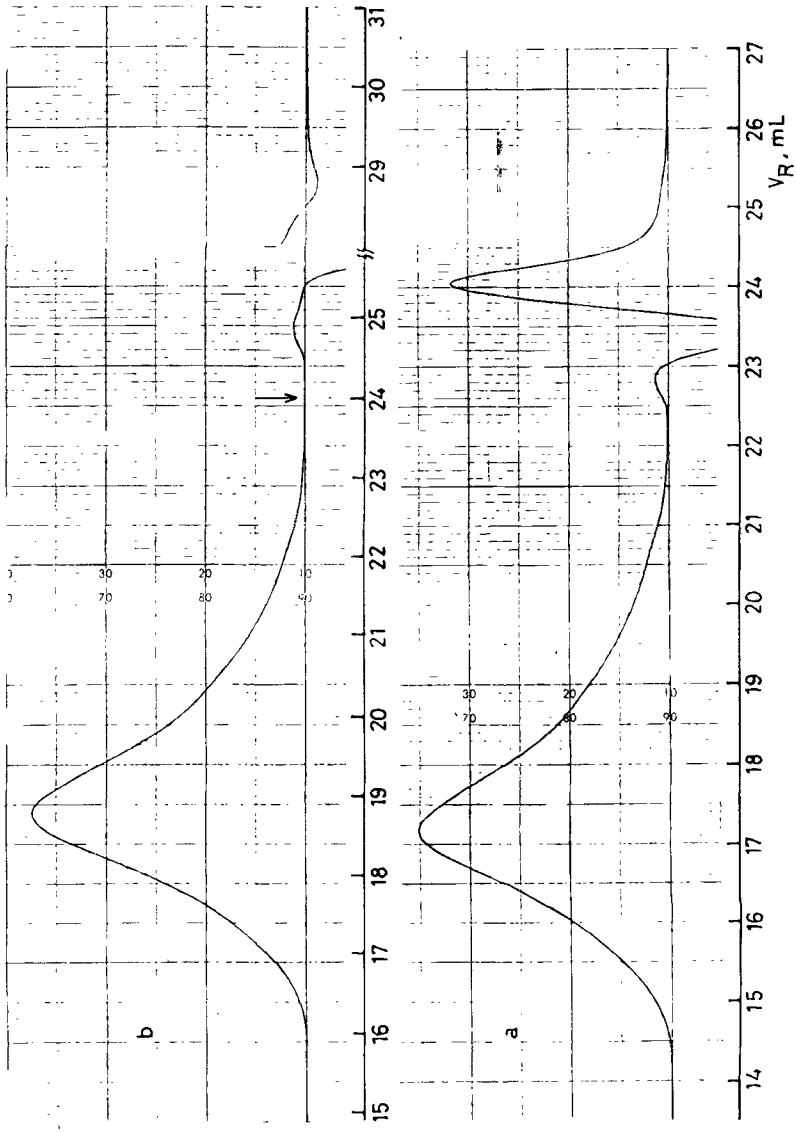

FIGURE 4 Chromatograms of PS-2 obtained with (a) column system A and (b) column system B.

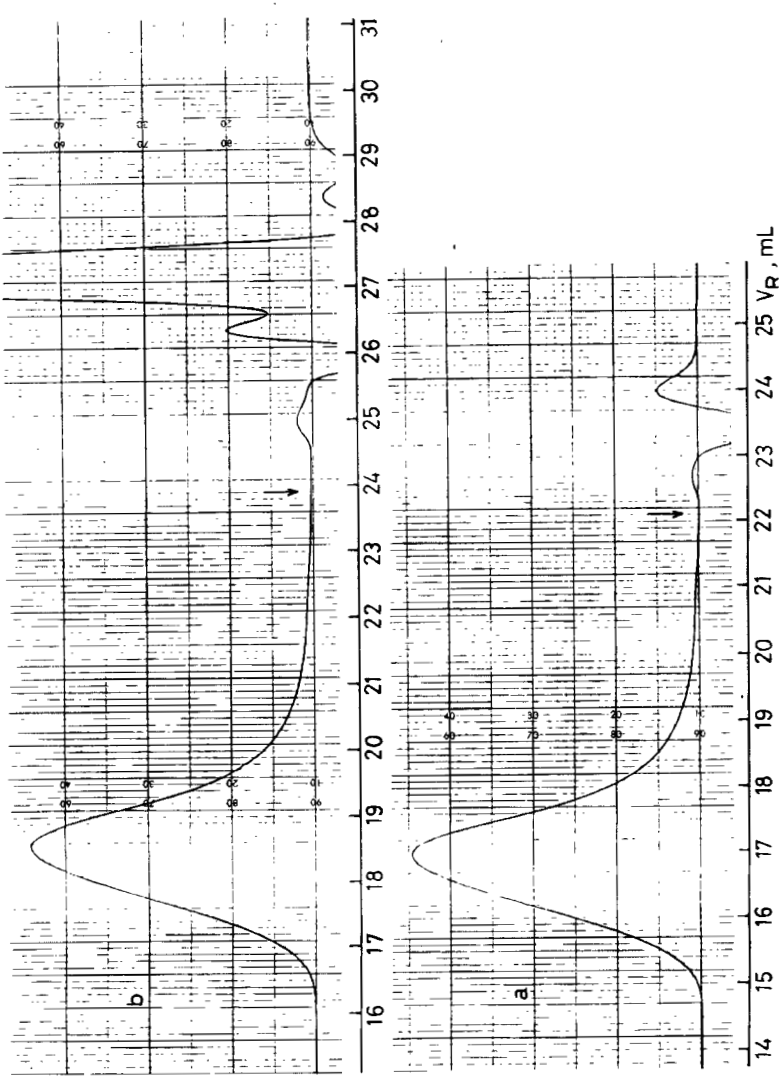

FIGURE 5 Chromatograms of reprecipitated SRM 706 PS obtained with (a) column system A and (b) column system B.

Although baseline separation was attained in both column systems for PS-1 (Fig. 3) and purified SRM 706 PS (Fig. 5), MM at the end of the polymer chromatogram was not the same in both column systems. MM at the end of the polymer chromatogram for column system B was higher than that for column system A. This difference is due to the increase of the resolution at the low-MM range by the connection of a Shodex SEC KF 800D column.

CONCLUSION

Polymer samples containing low-MM materials showed lack of baseline separation between the end of the polymer chromatograms and the beginning of the solvent peaks, which affects M_n reproducibility. The connection of a "Solvent-Peak Separation" column to polymer separation columns had the distinct effect of separating the polymer chromatogram from the solvent peaks. The connection of this short column did not change the shape of the calibration curve.

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