

Note

Determination of molecular-weight distribution of polymers by microcolumn exclusion chromatography*

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The use of microcolumn exclusion chromatography (MEC) for the investigation of the molecular-weight distribution (MWD) of polymers seems very promising. Low consumption of the sorbent ($\approx 50 \mu\text{g}$) and the solvent ($\approx 50\text{--}100 \mu\text{l}$) not only greatly reduces the cost of the analysis but also permits the use of a variety of solvents (including very pure solvents and those that are not readily available) and avoids the dangers of toxicity and fire. Taking as an example the separation of a mixture of polystyrene (PS) standards, it has been shown¹ that MEC systems can be developed (column diameter 0.6 mm) the performance of which is as high as that of conventional exclusion chromatographic columns (diameter 4.0 mm).

The aim of the present note is to describe a simple, reliable and precise system of MEC for the determination of the MWD of polymers.

Experiments were carried out with a microcolumn MSFP-3 chromatograph (Novosibirsk Institute of Organic Chemistry, Siberian Department of the Academy of Sciences of the U.S.S.R.). To increase the reproducibility of retention volumes a pump was prepared having a chamber volume of $300 \mu\text{l}$ and a precision calibrated plunger. A gear with a micrometer screw ensured to within 0.5% a constant volume rate of solvent injection. The columns were prepared from PTFE capillary tubes (0.6–0.65 mm I.D. and 0.7 mm O.D). They were packed with microspherical silica gel sorbents LiChrospher Si 100 (pore diameter = 100 \AA , particle diameter = $5 \mu\text{m}$) (1) and LiChrospher Si 1000 (pore diameter = 1000 \AA , particle diameter = $10 \mu\text{m}$) (2), from an aqueous suspension prepared in an ultrasonic disperser as described in ref. 2 at a rate of $67 \mu\text{l}/\text{min}$ (the pressure increasing to 70–80 atm). To increase the efficiency of the columns the sorbents were fractionated by sedimentation and fractions with particle diameter of $7 \pm 1 \mu\text{m}$ were used. The height equivalent to a theoretical plate of the columns was $35 \mu\text{m}$.

It has been shown¹ (Fig. 1) that a mixture of sorbents 1 and 2 in the ratio 2:3 permits the separation of PS over the MW range from 10^3 to $2 \cdot 10^6$. To increase the precision and simplify the calculations of MWD, a column was packed with a mixture of these sorbents which gave a linear calibration dependence (LCD) of retention volumes on $\log M$. On the basis of calibration dependences obtained for

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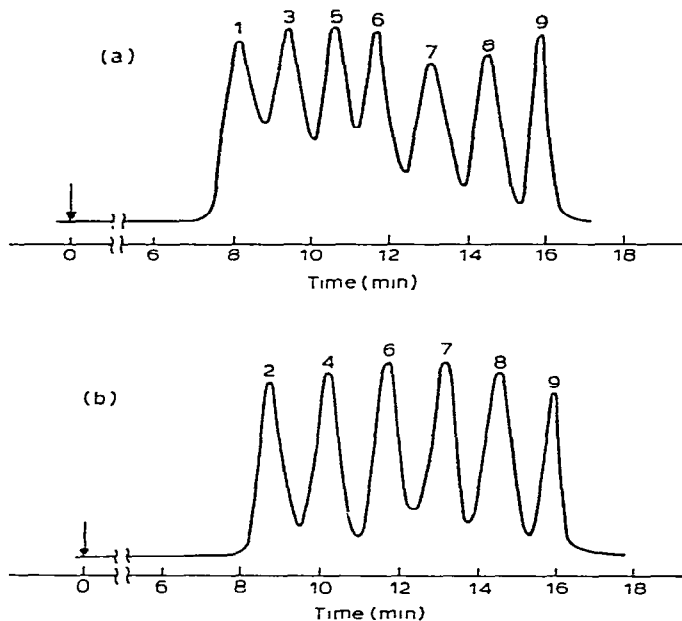


Fig. 1. Chromatograms of two mixtures (a,b) of PS standards. Column (300×0.6 mm) packed with a mixture of LiChrospher Si 100 and Si 1000 sorbents (2:3). Eluent: Methylene chloride; flow-rate $4.6 \mu\text{l}/\text{min}$. Sample volume: $0.5 \mu\text{l}$ ($5 \text{ mg}/\text{ml}$). Detection at $\lambda = 260 \text{ nm}$. M_w : $2.61 \cdot 10^6$ (1); $8.67 \cdot 10^5$ (2); $4.11 \cdot 10^5$ (3); $2.00 \cdot 10^5$ (4); $1.11 \cdot 10^5$ (5); $3.3 \cdot 10^4$ (6); 10^4 (7); $2.1 \cdot 10^3$ (8); 78 (9) (benzene).

each of these sorbents, their ratio in the mixture that gave a LCD to within 0.2% over the range of M from $3 \cdot 10^3$ to 10^6 was calculated³. The experimental calibration dependence obtained on a 300×0.6 mm column (efficiency 9500 plates) packed with this mixture of sorbents was in good agreement with the theoretical dependence and was strictly linear over this MW range (Fig. 2).

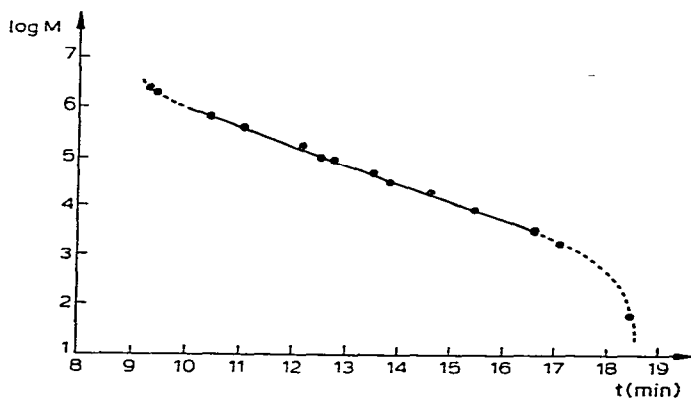


Fig. 2. Retention times vs. logarithm of the molecular weight of PS standards. Column (330×0.6 mm) packed with a mixture of LiChrospher Si 100 and Si 1000 sorbents. Eluent: methylene chloride; flow-rate $4.6 \mu\text{l}/\text{min}$. Sample volume: $0.3 \mu\text{l}$ ($1 \text{ mg}/\text{ml}$).

The chromatograms of PS standards obtained on this column exhibit asymmetric peaks, resulting in low values of average MW. This asymmetry is probably due to spreading in the detector as is shown by the results of our investigation of spreading in the cell. In separate experiments it was found that the concentration dependence of retention volumes is absent for PS with MW of 867,000 and 10,000 at concentrations of up to 1 mg/ml and 4–5 mg/ml respectively. To obtain true MWD it was necessary to correct for instrumental spreading.

MEC was used to determine the MWD of a PS standard, PS-706 (U.S. National Bureau of Standards)⁴. The MWD of this sample calculated from a chromatogram corrected for instrumental spreading⁵ and the values of M_w and M_n found from it are in good agreement with the literature data (Table I). The reproducibility of the determination was $\approx 5\%$.

TABLE I
CHARACTERISTICS OF SAMPLE PS-706

	MEC	According to ref. 4
M_n	$(148 \pm 5) \cdot 10^3$	$136.5 \cdot 10^3$
M_w	$(273 \pm 5) \cdot 10^3$	$(278 \pm 5) \cdot 10^3$

It has been shown that MEC can be used to analyse the MWD of polymers with a precision comparable to conventional EC but with an approximately hundred-fold decrease in the consumption of the sorbent and the eluent and a corresponding increase in sensitivity.

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