Macroreticular polyacrylamide gel particles for aqueous high performance gel permeation chromatography of poly(ethylene oxide)

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We have been investigating the preparation of macroporous gel particles formed in the copolymerization of acrylamide and *N*,*N*-methylene-bisacrylamide in an inverse suspension process. These experiments have been confined to copolymerizations in which the crosslinking agent is the major monomeric component by weight. Our studies of particle preparation are still in progress, and details will be reported when our investigations of the dependence of the porosity and rigidity of the particles on the polymerization conditions have been completed. The potential of these macroreticular gel particles for the column chromatography of water-soluble polymers has been tested. We present here the extremely promising initial results obtained in separations by high performance gel permeation chromatography (*HP*–g.p.c.).

Experimental

After the reaction product had been processed, the dry gel was separated with an Alpine Multi-Plex Zig-Zag Classifier (Department of Chemical Engineering). The air classifier settings were chosen to give a narrow particle size distribution with particle diameters in the range 7–12 μm. Scanning electron micrographs (see *Figure 1*) suggest that some particles are outside this size range, an observation also reported when classifying porous polystyrene gel particles[1]. The micrographs indicate that the particles are almost spherical with a narrow size distribution. The extent of porosity at the particle surface may be assessed from the micrograph of a single particle. Observations by optical microscopy suggested that the diameter of a dry particle increased by a factor $\leqslant 1.15$ on swelling with water.

The dry gel particles were dispersed in methanol, and this slurry was packed into a column (20×0.8 cm i.d.) at a pressure of about 2000 lbf/in^2 (1 lbf/in$^2 \equiv 6894.8$ N/m^2) according to the technique reported by Bristow *et al.*[2]. *HP*-g.p.c. separations were performed with a Perkin-Elmer Model 1220 positive displacement syringe pump employing distilled water as eluent. Solutions (25 μdm^3) of individual solutes were injected with an off-column syringe–septum arrangement as described in ref 1. Detection of solutes was performed with an LDC Refracto Monitor Model 1107 (cell volume = 0.5 μdm^3, aqueous reference). The samples of poly(ethylene oxide) designated PEO were narrow distribution TSK standards kindly supplied by Dr F. P. Warner, Polymer Laboratories Ltd, Church Stretton, Shropshire, UK. The samples of poly(ethylene glycol) are designated PEG with a number which is the molecular weight provided by the suppliers (Shell Chemicals, BDH). The calibration curve was established at a flow rate of 1 cm^3 min^{-1} with a PEG concentration of 0.5% (w/v) and a PEO concentration of 0.25% (w/v). Column efficiencies were determined with ethanol having a concentration of 0.5% in an injection volume of 25 μdm^3. Plate number was calculated from an experimental chromatogram by the width at half height method.

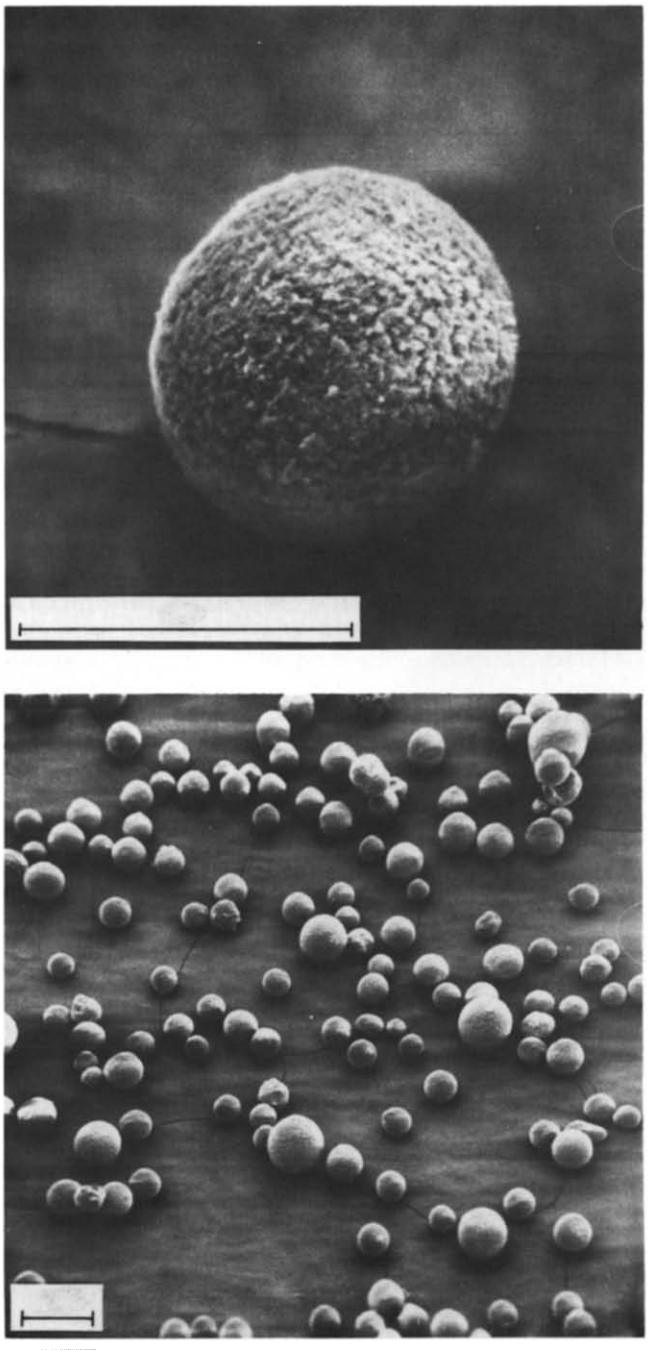

Figure 1 Scanning electron micrographs of polyacrylamide gel particles. Scale bars: upper micrograph, 10 μm; lower micrograph, 20 μm

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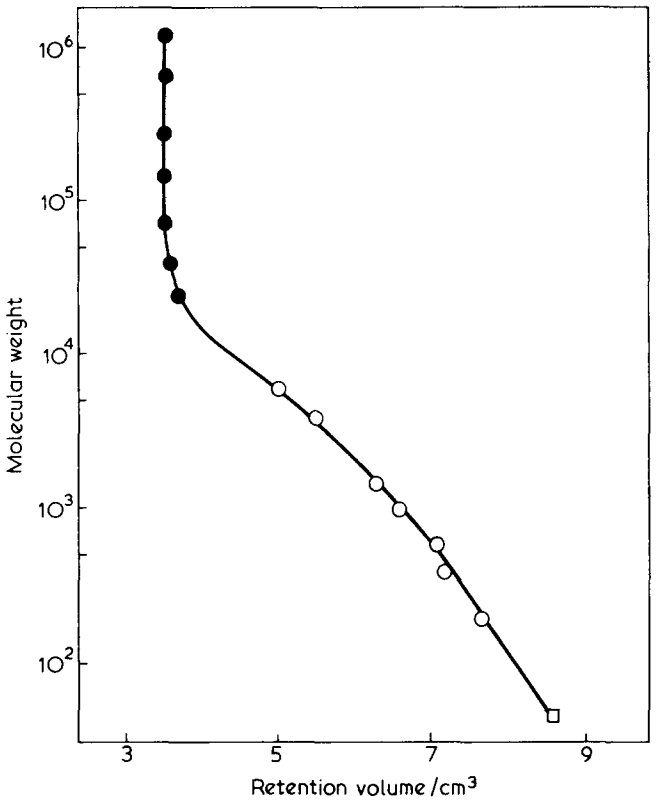

Figure 2 Molecular weight calibration curve for g.p.c. column containing polyacrylamide gel particles: ●, PEO; ○, PEG; □, ethanol

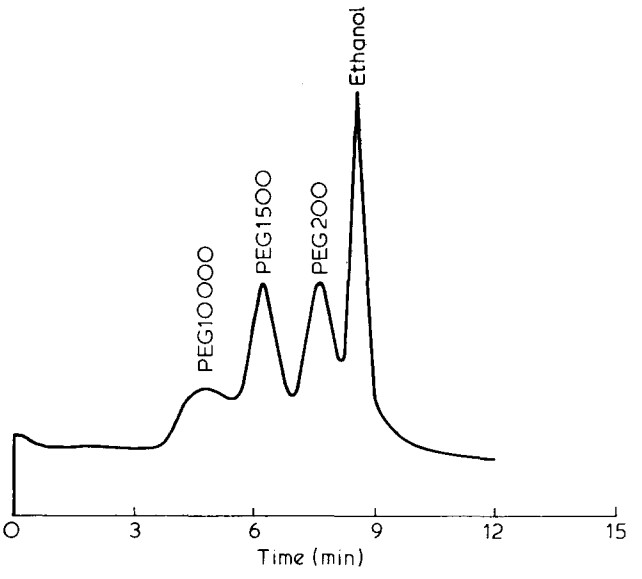

Figure 3 Chromatogram showing resolution of poly(ethylene glycol) samples and ethanol by *HP*-g.p.c. with polyacrylamide gel particles

Results

The calibration curve established with PEG and PEO samples as shown in *Figure 2* suggests a useful separation range of over two decades in molecular weight. The calibration curve suggests that the gel particles have high pore volume, since the ratio of the retention volume of PEG200 to the interstitial (or void) volume of the column is about 2.2. Plate numbers for ethanol over the flow rate range 0.4 to 1.0 cm^3 min^{-1} were between 17000 and 18500 plates m^{-1}. This high column efficiency was confirmed by the resolution of a 'cocktail' of three PEG samples and ethanol in 10 min as shown in *Figure 3*. These initial results suggest that *HP*-g.p.c. separations of polymers may be accomplished with macroreticular polyacrylamide gel particles having a diameter of about 10 μm. High resolution separations with these microparticulate gels in short low capacity columns are achieved much more quickly than in gel filtration separations with soft homogeneously crosslinked polyacrylamide xerogels which have high swelling and poor mechanical strength[3].

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REFERENCES

1 Dawkins, J. V., Stone, T. and Yeadon, G. *Polymer* 1977, **18**, 1179
2 Bristow, P. A., Brittain, P. N., Riley, C. M. and Williamson, B. F. *J. Chromatogr.* 1977, **131**, 57
3 Kremmer, T. and Boross, L. 'Gel Chromatography. Theory, Methodology, Applications', Wiley, New York, 1979