High performance g.p.c. with crosslinked polystyrene gels: influence of particle size on the polydispersity of high polymers

John V. Dawkins, Tadeusz Stone* and Graham Yeadon
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK
Frank P. Warner
Polymer Laboratories Limited, Essex Road, Church Stretton, Salop, UK
(Received 5 April 1979)

INTRODUCTION

The separation of spherical crosslinked polystyrene gel particles into fractions having average particle diameters in the range 10–40 μm was described in a previous paper[1]. The performance in gel permeation chromatography (g.p.c.) of columns containing these particles was determined with small molecules and a non-permeating polystyrene standard. Plate height results for these solutes as a function of eluent flow rate u suggested that gel particles with narrow size distributions were preferred in order to minimize chromatogram broadening due to solute dispersion in the mobile phase. A homogeneous bed of spherical particles having a narrow size distribution is advantageous from a practical viewpoint since column permeability will be maximized.

The study of the influence of particle size distribution on g.p.c. performance was restricted to gel particles with small pore diameters, which were suitable for separating solutes with molecular weights up to 2000[1]. Columns containing such particles having diameters of about 5–10 μm are useful in separations of oligomers, as shown by the high resolution experiments of Kato, Kido, Watanabe, Yamamoto and Hashimoto[2] who obtained multipeak chromatograms in order to identify individual oligomeric components. Chromatograms for high polymers are rarely multimodal, and the speed of separation and the precision of the molecular weight distribution calculated from the chromatogram are of greater importance than the resolution of individual components[3]. We have now examined the g.p.c. performance of columns containing spherical crosslinked polystyrene gel particles having narrow size distribution and covering a range of pore diameters, and in this communication we describe results for the polydispersity of a broad distribution polystyrene as a function of particle diameter and eluent flow rate.

EXPERIMENTAL

Batches of gel were prepared by the procedures described elsewhere[1]. Gels with narrow particle size distributions which were measured with a Coulter Counter were produced by air classification and were packed into columns, as described elsewhere[1]. Number-average and weight-average particle diameters, s_n and s_w, respectively, as defined in ref 1, were calculated from the particle size distributions and are shown in *Table 1*. A series arrangement of four g.p.c. columns was used, containing crosslinked polystyrene gels with exclusion limits of 10^6, 10^5, 10^4 and 10^3 Å (10 Å ≡ 1 nm). The column dimensions were 30 × 0.77 cm (10 μ), 25 × 0.75 cm (15 μ), and 60 × 0.77 cm (20 μ). The g.p.c. instrumentation and experimental procedures have been described in detail[4]. A syringe-septum injector was used at pressures below 1500 lbf/in^2 (1 lbf/in^2 ≡ 6894.8 N/m^2). The u.v. detector (254 nm, 8 μdm^3) was used on maximum sensitivity. The polydisperse polystyrene PSGY2 was prepared by a radical chain polymerization of styrene at 333K. The polymerization was performed to low monomer conversion under carefully controlled conditions, as described elsewhere[4]. The injected solutions in g.p.c. had polystyrene concentrations of 0.2% (w/v) in tetrahydrofuran with tetraphenylethylene (~0.01%, w/v) added as internal standard. The injection volumes were 40 μdm^3 for calibration with polystyrene standards and 80 μdm^3 for polystyrene PSGY2. Number-average and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, respectively, were calculated from a chromatogram with the program of Croucher[5], based on the method of Pickett, Cantow and Johnson[6].

RESULTS AND DISCUSSION

Scanning electron micrographs demonstrated that the gel particles were spherical. Size distributions for the gel particles, constructed by drawing a curve through the weight

Table 1 Average particle diameters and polydispersities of gel particles and g.p.c. results for columns of gel particles at an eluent flow rate of 1 cm^3 min^{-1}

Gel	s_n (μm)	s_w (μm)	s_w/s_n	L^c (cm)	Pressure drop (lbf/in^2)	N^d (plates m^{-1})	Separation time (min)	$[\bar{M}_w/\bar{M}_n]$ (PSGY2)
10 μ^a	9.84	11.89	1.21	120	625	30 000	45	1.69
15 μ	15.30	17.56	1.15	100	~130	16 000	35	1.74
20 μ^a	20.15	23.11	1.15	240	160	6000	90	1.79
PSCC^b	–	–	–	480	~120	–	180	1.85

[a] Columns of PLgel (tradename of Polymer Laboratories Ltd)
[b] Columns of Styragel (tradename of Waters Associates) at Polymer Supply and Characterisation Centre, RAPRA, Shawbury, Shrewsbury, UK
[c] Total column length
[d] Minimum plate number determined for each column wich dichlorobenzene

---

* Present address: TBA Industrial Products, Stanhope Road, Camberley, Surrey

0032–3861/79/091164–03\$02.00

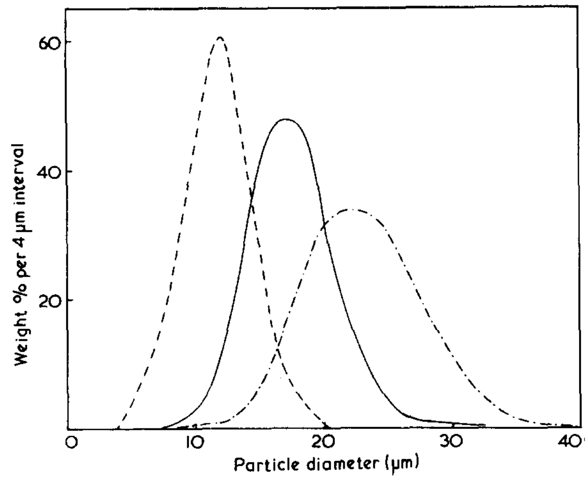

Figure 1 Weight fraction particle size distributions: — — —, 10 μ gel; ——, 15 μ gel; — · — · — · —, 20 μ gel

fractions at the midpoints of the 4 μm intervals, are shown in *Figure 1*. Values of the polydispersity s_w/s_n in *Table 1* demonstrate that the gels have narrow particle size distributions, in agreement with the previous results[1]. The dominant termination mechanism in the polymerization of styrene is radical combination[7,8] and so the polydispersity $[\bar{M}_w/\bar{M}_n]$ of polystyrene PSGY2 should be close to 1.5[9]. A comparison of the g.p.c. data in *Table 1* for the 20 μ and PSCC gel columns suggests that the 20 μ particles give a more accurate molecular weight distribution in a shorter separation time. Furthermore, the 20 μ gel columns retain the option of using low pressure (<300 lbf/in^2) instrumentation such as that developed by Waters Associates[10,11] because the narrow particle size distribution minimizes the resistance to fluid flow, so that fast separations at low pressures may be performed. The particle size distribution for Styragel particles in the PSCC columns is not known. The diameter of Styragel particles is claimed to be ~50 μm[12], but ARgeL particles which have a similar g.p.c. performance have s_w ~ 37 μm[1].

The g.p.c. results in *Table 1* demonstrate that the best column performance is obtained with the 10 μ gel columns, which are shorter than the 20 μ and PSCC gel columns and so give faster separations. The separation time may be lowered further by raising the eluent flow rate, and the dependence of $\ln[\bar{M}_w/\bar{M}_n]$ on u is shown in *Figure 2a*. This plot may be justified from theoretical considerations, as discussed in a previous paper[4]. The smallest particles are therefore advantageous for high speed separations. For example in *Figure 2a*, similar values for $[\bar{M}_w/\bar{M}_n]$ are obtained for the 10 μ gel columns (u = 2 cm^3 min^{-1}) and for the 20 μ gel columns (u = 0.5 cm^3 min^{-1}), but the 10 μ gel columns give separations eight times faster. It is evident in *Figure 2a* that the value of $[\bar{M}_w/\bar{M}_n]$ closest to the polydispersity expected from the polymerization mechanism is achieved with the 10 μ gel columns at the lowest practical flow rate (0.2 cm^3 min^{-1}) giving a separation time of 225 min. Therefore, at the same separation time, the 10 μ gel columns give a much more precise determination of $[\bar{M}_w/\bar{M}_n]$ than the traditional g.p.c. approach as exemplified by the PSCC gel columns. The reduction in column performance as u increases results from the g.p.c. mass transfer mechanism which becomes the dominant contributor to chromatogram broadening for high polymers at fast flow rates[4]. The plot in *Figure 2b* for polystyrene PSGY2 is consistent with this view since the mass transfer mechanism is proportional to the square of s_w, taking a value of D_m for polystyrene PSGY2 ($\bar{M}_n$ = 76 000) to be 4.63 x 10^{-7} cm^2 s^{-1} (see ref 4). In *Table 1* the decrease in the polydispersity of polystyrene PSGY2 as s_w is lowered results mainly from a decrease in $\bar{M}_w$, the change in $\bar{M}_n$ being much less significant. This may be explained by the dependence of $[\bar{M}_w/\bar{M}_n]$ on the mass transfer term in *Figure 2b*. Chromatogram broadening due to mass transfer will be more prevalent for the longer chains having lower values of D_m. Therefore, it is suggested that chromatogram broadening for the high molecular weight tail should be greater than for the low molecular weight tail of a distribution and so $\bar{M}_w$ will change more than $\bar{M}_n$ as s_w is raised.

In conclusion, the most precise values of polydispersity for high polymers are obtained at low eluent flow rates (u ~ 0.1 cm^3 min^{-1}) with columns containing the smallest particles, e.g. 10 μ gel. High speed separations at faster flow rates should also be performed with the smallest particles but require high pressure instrumentation even though the small particles are contained in short columns. An increase in particle size gives a significant fall in column performance, but columns containing larger particles such as 20 μ gels do not require high pressure instrumentation.

ACKNOWLEDGEMENTS

The authors thank Mr R. E. Buxton and Mr D. Pinder, Department of Chemical Engineering, for helpful discussions and for assistance with air classification and Coulter Counter measurements. This research was supported by grants from Applied Research Laboratories, and from the Science Research Council in collaboration with the SRC-supported Polymer Supply and Characterisation Centre at RAPRA, Shawbury, Shrewsbury, UK. The authors thank

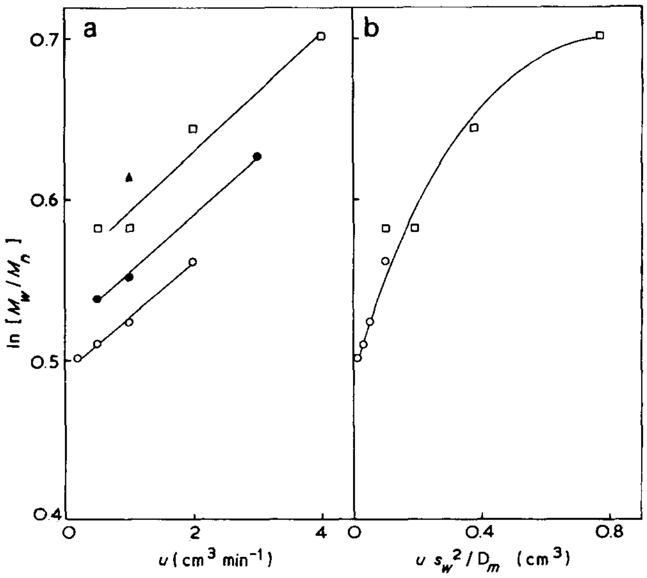

Figure 2 Dependence of polydispersity of polystyrene PSGY2 on eluent flow rate and on the mass transfer contribution to chromatogra broadening: ○, 10 μ gel; ●, 15 μ gel; □, 20 μ gel; ▲, PSCC gel

Mr L. J. Maisey at RAPRA for the g.p.c. determination of the polydispersity of polystyrene PSGY2 with the PSCC columns.

REFERENCES

1 Dawkins, J. V., Stone, T. and Yeadon, G. *Polymer* 1977, **18**, 1179
2 Kato, Y., Kido, S., Watanabe, H., Yamamoto, M. and Hashimoto, T. *J. Appl. Polym. Sci.* 1975, **19**, 629
3 Dawkins, J. V. and Yeadon, G. in 'Developments in Polymer Characterisation – 1' (Ed. J. V. Dawkins), Applied Science Publishers, London, 1978, Ch. 3
4 Dawkins, J. V. and Yeadon, G. *Polymer* 1979, **20**
5 Croucher, T. G. *PhD Thesis* Loughborough University of Technology (1976)
6 Pickett, H. E., Cantow, M. J. R. and Johnson, J. F. *J. Appl. Polym. Sci.* 1966, **10**, 917
7 Berger, K. C. and Meyerhoff, G. *Makromol. Chem.* 1975, **176**, 1983
8 Berger, K. C. *Makromol. Chem.* 1975, **176**, 3575
9 Peebles, L. H. 'Molecular Weight Distributions in Polymers', Wiley–Interscience, New York 1971
10 Moore, J. C. *J. Polym. Sci. (A)* 1964, **2**, 835
11 Maley, L. E. *J. Polym. Sci. (C)* 1965, **8**, 253
12 Vivilecchia, R. V., Lightbody, B. G., Thimot, N. Z. and Quinn, H. M. *J. Chromatogr. Sci.* 1977, **15**, 424

Electrical resistivity of PVC—Cu composites

Swapan K. Bhattacharyya
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
(Received 3 April 1979)

In the past few years research has been conducted to enhance the electrical resistivity of polymers by impregnation of metallic fillers. Conductivity of such polymer composites depends on the concentration of filler[1,2], size ratio of the polymer to metal particles[3–5] and also on the oxide content of the filler particles[4,6]. Matushita *et al.*[7] have made extensive investigations on hot-pressed polystyrene–silver composites and have shown that resistivity of the system could be controlled by compaction pressure through densification of the polymer matrix. The electrical conductivity as well as the strength of the composite shows much lower values when compacted at a lower pressure[8] than that could be obtained by conventional processing[9]. In the present work, a systematic investigation has been made on the dependence of electrical resistivity of poly(vinyl chloride)–copper (PVC–Cu) composites on the compacting pressures at which the composites were prepared.

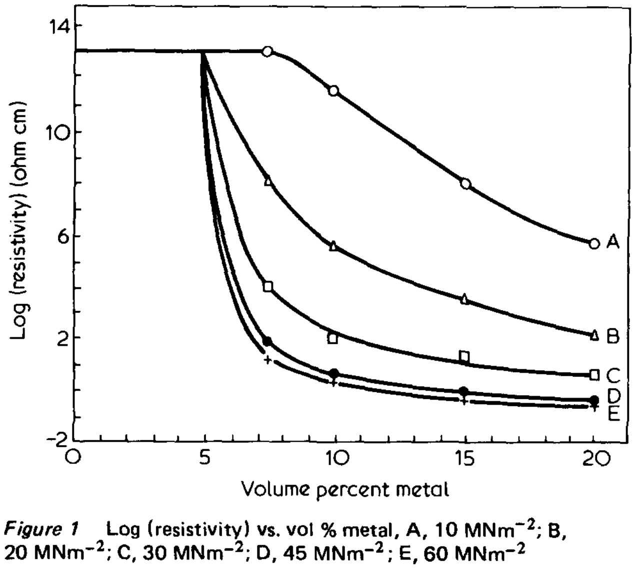

Figure 1 Log (resistivity) vs. vol % metal, A, 10 MNm^{-2}; B, 20 MNm^{-2}; C, 30 MNm^{-2}; D, 45 MNm^{-2}; E, 60 MNm^{-2}

PVC and copper powders of average particle size 128 and 7 μm were thoroughly mixed by tumbling and compacted at a temperature of 130°–140°C in a steel cylindrical die at a desired pressure. Rectangular specimens (approximately 1.5 x 1.0 x 0.7 cm) were machined out from the briquettes so formed. Prior to the measurement of electrical resistivity these specimens were annealed at 50°C in an oven for 10 days to achieve better reproducibility of the resistivity values[10]. Details of the method of preparation, measurement of electrical resistivity and Vickers hardness of the composites has been reported elsewhere[4,9]. Porosity was calculated from the experimental and the theoretical density values.

Resistivity as a function of metal concentration at different compacting pressures is shown in *Figure 1*. The sharp drop in the resistivity value particularly at higher compacting pressure has been explained on the basis of formation of intermetallic contacts[1,3–5]. Since resistivity of the composites below critical metal loading is controlled by the probability of the metal–ion contact formation[4], we have made experiments only beyond the metal concentration where complete formation of the segregated network is almost achieved. It is observed that at much lower pressure the resistivity vs. metal concentration curve shows a gentle fall because of the changed contact condition due to the improper coalescence of the matrix phase[6,8]. With increasing

Table 1 Porosity and Vickers hardness values of PVC–Cu composites at various compacting pressures

	At 5 volume percent		At 15 volume percent	
Compacting pressure (MNm^{-2})	Porosity (%)	Vickers hardness (kg/mm^2)	Porosity (5)	Vickers hardness (kg/mm^2)
10	25–35	2–5	20–25	4–8
20	15–20	2–6	10–20	4–10
30	8–10	4–8	4–8	14–18
45	3–4	14–16	3–4	18–20
60	3–4	14–16	3–4	18–20

0032-3861/79/091166–02$02.00