

Letter

Gel permeation chromatography of crosslinked particles prepared by emulsion polymerization

Grubisic, Rempp and Benoit¹ have found that the elution behaviour of many homopolymers and copolymers in gel permeation chromatography (g.p.c.) is governed by a molecular property proportional to the product of intrinsic viscosity and molecular weight $[\eta]M$ against elution volume, i.e. they have shown that a plot of $[\eta]M$ established using a set of well characterized samples with narrow size distribution, will serve as a 'universal' calibration for a given set of columns. The introduction of the radius of the equivalent hydrodynamic sphere^{1,2}, R_η yields:

$$[\eta]M = 2.5 \left(\frac{4}{3} \pi R_\eta^3 \right) N_A = 2.5 V_\eta N_A$$

where N_A is Avogadro's number and V_η is the hydrodynamic volume. Thus the results of Grubisic *et al.*¹ are consistent with a separation in g.p.c. which is governed by the hydrodynamic volume.

There is some doubt as to whether the 'universal' calibration can be successfully applied to highly branched systems³⁻⁵. Most recently⁵ Ambler and McIntyre suggest that highly randomly branched poly(styrene/divinyl benzene) fractions do not conform to a 'universal' calibration established using linear polystyrene standards.

Here we report on a study g.p.c. of well characterized crosslinked poly

(styrene/divinyl benzene) particles produced by emulsion polymerization under conditions which lead to particles which are spherical in shape and almost monodisperse in size⁶. It is possible to remove surfactants and electrolytes from such systems by ion exchange⁷ to give particles which provide useful models for a variety of research problems⁸. Following other authors⁹ we refer to such particles as microgels.

Experimental

Preparation of microgels. A procedure similar to that described by Woods *et al.*⁶ was used to prepare the latices. The materials used in the emulsion polymerizations were: styrene (BDH laboratory reagent); divinyl benzene (Koch-Light reagent grade); anionic surfactant, dodecyl benzene sulphonate containing Na_2SO_4 (Koch-Light Ultrawet K); non-ionic surfactant, poly(ethylene oxide)isooctyl phenyl ether (BDH Triton X-100); potassium persulphate as initiator; sodium thiosulphate as activator; sodium hydroxide and distilled water. The compositions of the reaction mixtures and temperatures of polymerization are given in *Table 1*. At the end of the reaction, emulsifier and electrolyte were removed from the reaction products by mixed-bed ion exchange using carefully purified Amberlite resins. The microgels were isolated for studies in other solvents by freeze drying.

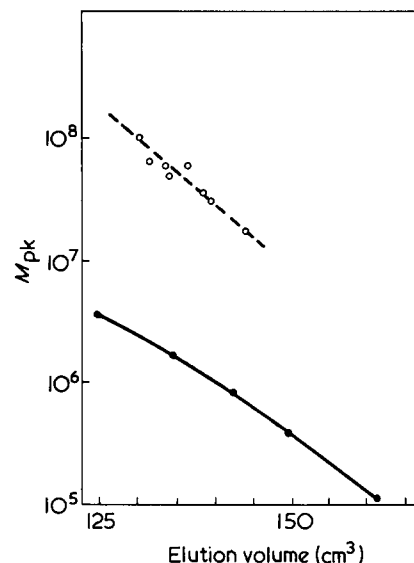


Figure 1 Plot of peak molecular weight, M_{pk} , versus elution volume for linear polystyrene standards (●) and for microgels (○)

Electron microscopy. Drops of purified latex were dried on a carbon substrate supported by a copper grid. Specimens were shadowed with platinum/carbon and then observed and photographed in an AEI 6G electron microscope. As observed in previous studies⁸ the particles from each sample were spherical in shape and in most cases had a narrow distribution of sizes. The average sizes of particles were de-

Table 1 Electron microscopy for different emulsion polymerization conditions

Sample	H ₂ O (cm ³)	Styrene (cm ³)	Divinyl benzene (cm ³)	Ultrawet K (cm ³)*	Triton X (cm ³)*	K ₂ S ₂ O ₈ (cm ³)*	Na ₂ S ₂ O ₃ (cm ³)*	0.1 M NaOH (cm ³)	T(°C)	$(\bar{D}_n^3)^{1/3}$ (nm)	$\bar{M}_n \times 10^{-7}$	$\bar{M}_w \times 10^{-7}$	\bar{M}_w/\bar{M}_n	$M_{pk} = (\bar{M}_w \bar{M}_n)^{1/2} \times 10^{-7}$
1	400	76	8	4	12	16.6	—	—	80	66.6	9.8	10.8	1.10	10.3
2	400	76	8	4	12	16.6	—	—	80	66.2	9.7	10.5	1.09	10.1
3	400	76	8	4	12	16.6	—	—	60	56.1	5.9	7.1	1.20	6.5
4	384	76	12	6	12	16.6	10	—	70	55.3	5.7	6.6	1.17	6.1
5	394	76	12	6	12	16.6	—	—	80	55.2	5.6	6.4	1.13	6.0
6	394	76	12	6	12	16.6	—	—	70	51.7	4.6	5.5	1.19	5.0
7	392	76	12	8	12	16.6	—	—	80	46.0	3.3	4.0	1.24	3.6
8	315	76	20	20	12	16.6	20	35	94	43.2	2.7	3.5	1.29	3.1
9	352	76	20	20	12	16.6	—	20	94	34.6	1.4	2.2	1.58	1.7

* Concentrations of solutions used were: Ultrawet K, 0.1 g/cm³ of H₂O; Triton X, 0.18 g/cm³ of H₂O; K₂S₂O₈, 0.03 g/cm³ of H₂O; Na₂S₂O₃, 0.03 g/cm³ of H₂O

terminated from measurements on enlarged prints. Measurements were also made on unshadowed specimens for comparison. Approximately 500 particles were measured for each specimen and average molecular weights were determined by assuming that the density of each particle was the same as that of poly(styrene/divinyl benzene) copolymer in the bulk state ($\rho = 1.06 \text{ g/cm}^3$)⁹.

The results of the electron microscopical characterizations of the particles are presented in *Table 1*, where $(\overline{D}_n^3)^{1/3}$ is the root mean cube diameter, \overline{M}_n the corresponding number-average molecular weight and \overline{M}_w the weight-average molecular weight (calculated from $(\overline{D}_w^3)^{1/3}$).

Dilute solution studies. Exploratory studies were carried out with toluene, *N,N'*-dimethylacetamide, tetrahydrofuran and dimethyl formamide (DMF) solvents over a range of temperatures (20°–80°C). In all these solvents the particles were partly aggregated (as observed by light scattering and electron microscopy). The solvent eventually chosen, in which aggregation did not occur, was 0.1 molar lithium bromide in DMF at 80°C. This solvent has been used previously for g.p.c. investigation of polyelectrolytes^{10,11}.

Conditions for g.p.c. were as follows: 4 styragel columns each of length 1.22 m ranging in nominal pore size from 100 to 5×10^2 nm; solvent flow rate of 1 cm³/min; initial sample concentration of 2 g/dm³. Both linear polystyrene standards (Pressure Chemical Co. and Waters Associates) and the microgels were stu-

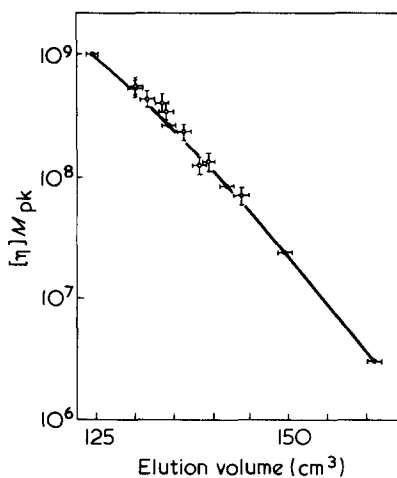


Figure 2 Comparison of a 'universal' calibration plot established using linear polystyrene standards (●) with values of $[\eta]M_{pk}$ for microgels (○)

died. The g.p.c. results are plotted semilogarithmically as M_{pk} against elution volume in *Figure 1*.

Intrinsic viscosities of the linear polystyrene standards and the microgels were measured in the g.p.c. solvent at 80°C by the usual methods. The results for the standards were similar to those found earlier¹¹. The semilogarithmic 'universal' calibration plots of $[\eta]M_{pk}$ against elution volume for the linear standards (full line) and the microgels (open circles) are given in *Figure 2*. The 'universal' calibration concept is very satisfactory. The results show that for the particles which are approximately spherically symmetrical

the original proposals of Grubisic *et al.* provide a sound working basis.

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