G.p.c. behaviour of hydrophobic beads with a double layer structure

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Several types of hydrophobic gel beads, consisting of an outer crosslinked layer and an inner non-crosslinked or lightly crosslinked part, have been prepared. When the ratio of the thickness of the outer layer to that of the inner part of a gel was small and the difference between crosslinking densities of both layers was sufficiently large, polymers of high molecular weight were excluded from gel beads and polymers of low molecular weight penetrated into gel beads. Thus, eluting a mixture of homologous polymers through the column packed with the gels, using an organic solvent as an eluent, resulted in the polymers being fractionated into two groups. This unusual behaviour of the gels is very similar to that previously reported for hydrophilic poly(vinyl alcohol) gel beads (Hirayama et al.) with a double layer structure.

INTRODUCTION

It was reported in a previous paper[1] that the behaviour of the hydrophilic beads prepared from poly(vinyl acetate) beads by partial saponification followed by crosslinking of the outer layer and saponification of the inner part was unusual compared with that of normal gels[2–5]. This was owing to the structure of the beads, which consisted of a crosslinked, thin outer layer and a non-crosslinked or lightly crosslinked inner part. Hydrophobic beads with a double layer structure were prepared from hydrophobic materials, e.g. poly(vinyl acetate) (PVAc) or polystyrene (PS), and the behaviour of the beads was examined.

EXPERIMENTAL

Preparation of gel beads

PVAc beads obtained by suspension-polymerization of vinyl acetate were saponified[1]. The resulting beads consisted of a poly(vinyl alcohol) (PVA) outer layer and a PVAc inner part. The beads were γ-irradiated at room temperature using ^{60}Co followed by saponification. The first type, A, of hydrophobic bead with a double layer structure was obtained from the saponified beads by acetylation[6] or after secondary irradiation at a small total dosage of γ-rays.

A second type of hydrophobic bead, B, was prepared from beads consisting of PVAc or copoly(vinyl acetate–butanediol divinyl ether) (BDVE) by partial saponification, followed by crosslinking with epichlorohydrin and acetylation with pyridine and acetic anhydride. The third type of hydrophobic bead, C, was prepared from copoly(styrene–divinyl benzene) by chloromethylation with chloromethyl ether[7], followed by crosslinking with sodium sulphide and sulphur.

The preparation methods of the three types of gels are diagrammatically described in *Figure 1*.

Gel permeation chromatography (g.p.c.)

G.p.c was carried out using the synthesized gel. Methyl alcohol was used as eluent with the A and B-gels, but ethyl acetate was used with the C gel. An homologous series of poly(ethylene glycol) and polystyrene were used as permeable substances. They are listed in *Table 1*. The calibration curves were obtained by plotting the average molecular weight against the peak elution volumes. The relation for the centre part of the curve, of slope α, was given as follows[8]:

$$\log M = \beta - \alpha(V_e/V_t)$$

where V_t is the total volume of gel bed and V_e is the eluting volume of a substance with molecular weight M. The excluded molecular weight, M_{lim}, was obtained by extrapolating the linear part of the $\log M$ *versus* V_e curve to $V_e = V_o$, where V_o is outer volume of the gel bed.

Swelling degree and solvent regain of gels

The measurements of swelling degree [Sd = wet bed (ml)/dry gel (g)] and solvent regain [Sr = solvent (g)/dry gel (g)] were carried out as previously reported[1]. Solvents used in the measurements were the same as those used in the g.p.c. operation.

Thickness ratio

The measurement of thickness ratio was carried out as previously reported[1]. Thickness ratio, r, is the ratio of the thickness of the outer layer to the radius of the inner part.

Elementary analysis

Chlorine contents of chloromethylated copoly(S–DVB) were measured using an improved type of combustion flask[9]. Chlorine and sulphur contents of C-type gels were measured using electron-microprobe X-ray analyser, EMx-SM(Shimazu Seisakusho).

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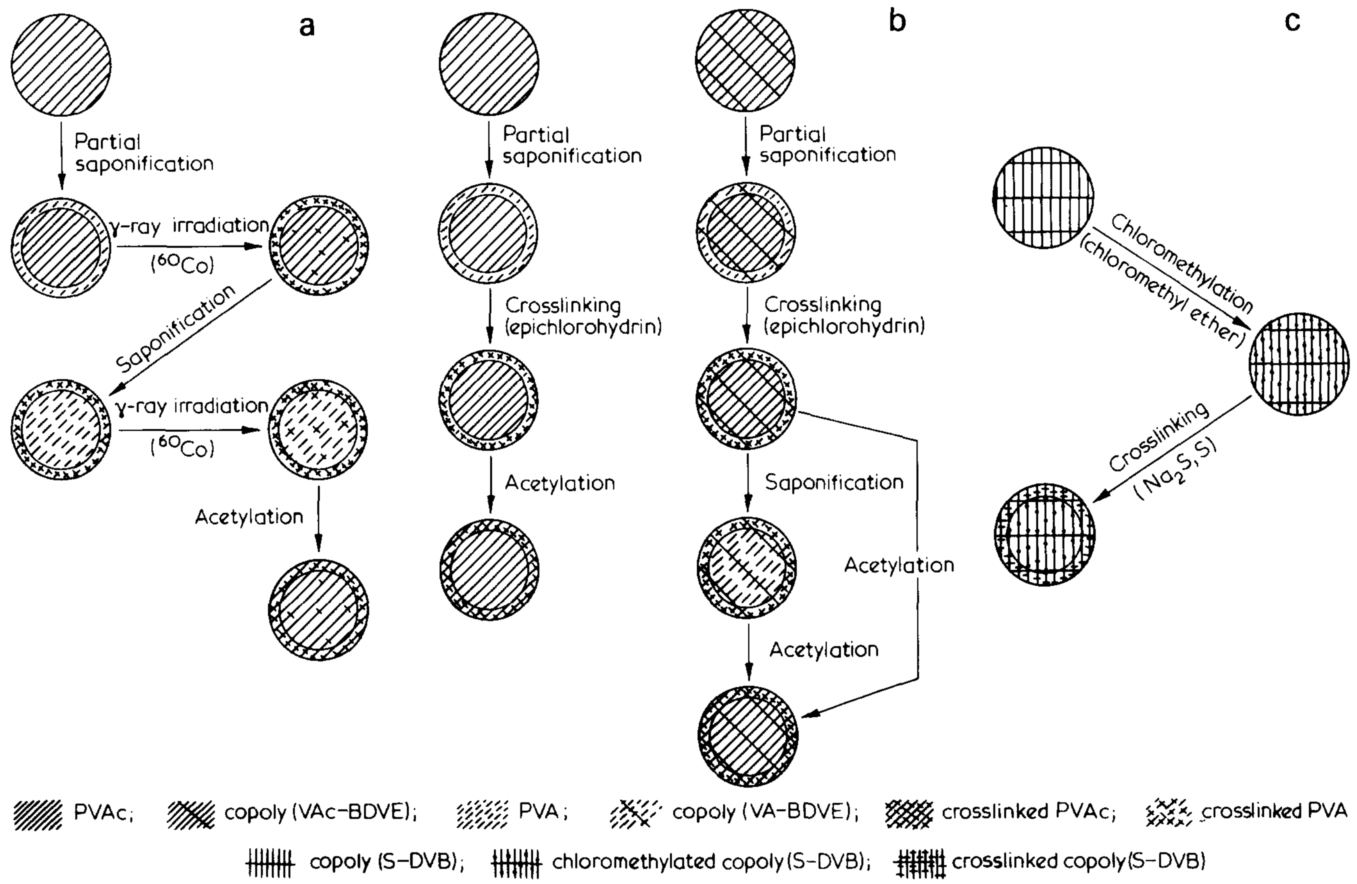

Figure 1 Schematic sketch of preparation method of A-type gels with a double layer structure; (b) schematic sketch of preparation method of B-type gels with a double layer structure; (c) schematic sketch of preparation method of C-type gels with a double layer structure

Table 1 Permeable substances

No.	Sample	$\bar{M}_n$	$\bar{M}_w$	Concentration
S1	EG	62		3
S2	DEG	106		3
S3	PEG – 200	203		3
S4	PEG – 500	480		3
S5	PEG – 700	700		3
S6	PEG – 1300	1280		3
S7	PEG – 1500	1520		3
S8	PEG – 2000	2300		3
S9	PEG – 3500	3400		3
S10	PEG – 8000	8100		3
S11	PEG – 10 000	10 000		3
S12	PEG – 20 000	21 000		3
S13	PEG – 20M	28 000		3
S14	PSt – 1	96 200	98 200	2
S15	PSt – 2	392 000	411 000	2

RESULTS AND DISCUSSION

Preparation conditions and properties of A-type gels are shown in *Table 2* and *Table 3*. Elution curves using A-3 gel and calibration curves for A-type gels are shown in *Figures 2* and *3*, respectively. A-type gels were obtained from the beads consisting of a PVA outer layer and a PVAc inner part, by primary γ-irradiation followed by saponification, secondary γ-irradiation, and acetylation. The inner part of the gel obtained by partial saponification followed by primary γ-irradiation at 10^6–10^7 röntgens (R) and saponification, consisted of PVA solution. Therefore, the crosslinking of gels by secondary γ-irradiation at a small total dosage would occur in the outer crosslinked PVA layer and in the inner PVA solution simultaneously. The concentration of PVA in the solution was about 1 g/dl. The value of M_{lim} equalled 200 000 when the solution was γ-irradiated at 10^7 R, however, a measurement of M_{lim} was impossible when γ-irradiated at 10^6 R, but was estimated for the inner PVA as being greater than 200 000. Meanwhile, the crosslinking of the crosslinked PVA outer layer by secondary γ-irradiation was negligible, because the dosage of secondary γ-irradiation was considerably less than that of primary γ-irradiation. Therefore, A-type gels are considered to be PVAc gels with a double layer structure which consists of a crosslinked outer layer and a lightly crosslinked inner part. A-5 and A-6 gels are different. These were primarily γ-irradiated at 10^8 R. The value of M_{lim} for the PVA obtained from the outer layer of these gels by γ-irradiation at 10^8 R was 3400, but the M_{lim} for the same PVA as obtained from inner PVAc of the gels, γ-irradiated at the same total dosage and subsequent saponification, was 20 000. Therefore, the difference in crosslinking densities between the outer layer and the inner part of A-5 and A-6 gels may be considered to be less than those of A-1, A-2, A-3 and A-4 gels. Thickness ratios of A-1 and A-2 gels, and A-3 and A-4 gels were 0.11 and 0.01, respectively. The α values of the former group were larger than those of the latter group. The difference in α value between A-1 and A-2 or A-3 and A-4 gels was caused by a difference in total dosage of secondary γ-irradiation. Hence, as total dosage increased, values for M_{lim} decrease, whereas α values increase. Large α values of A-5, A-6 gels were caused by a small difference between the crosslinking

Table 2 Preparation of PVAc gels with a double layer structure

Gel no.	Thickness ratio, r	Primary γ-irradiation			Secondary γ-irradiation		
		Dose rate (R/h)	Total dose (R)	Medium	Dose rate (R/h)	Total dose (R)	Medium
A-1	0.11	6.5×10^5	1.04×10^7	Water	1.25×10^4	1.05×10^4	Water
A-2	0.11	6.5×10^5	1.04×10^7	Water	1.20×10^5	1.00×10^5	Water
A-3	0.01	6.5×10^5	1.04×10^7	Water	1.25×10^4	1.05×10^4	Water
A-4	0.01	6.5×10^5	1.04×10^7	Water	1.20×10^5	1.00×10^5	Water
A-5	0.01	1.1×10^6	1.00×10^8	Water	1.05×10^5	1.05×10^5	Water
A-6	0.04	1.1×10^6	1.00×10^8	Water	1.05×10^5	1.05×10^5	Water

Table 3 Properties of PVAc gels with a double layer structure

Gel no.	Thickness ratio, r	Degree of swelling [wet (ml)/ dry gel (g)]	Solvent regain [methanol (g)/ dry gel (g)]	M_{lim}	α
A-1	0.11	18.0	4.7	11 200	1.5
A-2	0.11	12.7	4.7	7800	1.8
A-3	0.01	45.6	13.9	21 000	0.7
A-4	0.01	87.5	23.0	20 800	0.8
A-5	0.01	5.0	3.3	4800	1.9
A-6	0.04	5.4	2.1	3900	2.0

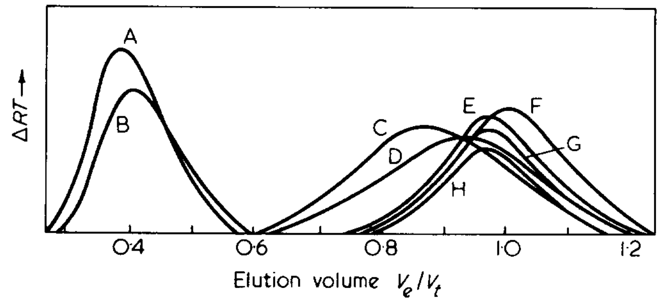

Figure 2 Elution diagrams of PEG on A-3 gel: A, S13; B, S12; C, S11; D, S9; E, S2; F, S1; G, S3,4; H, S6

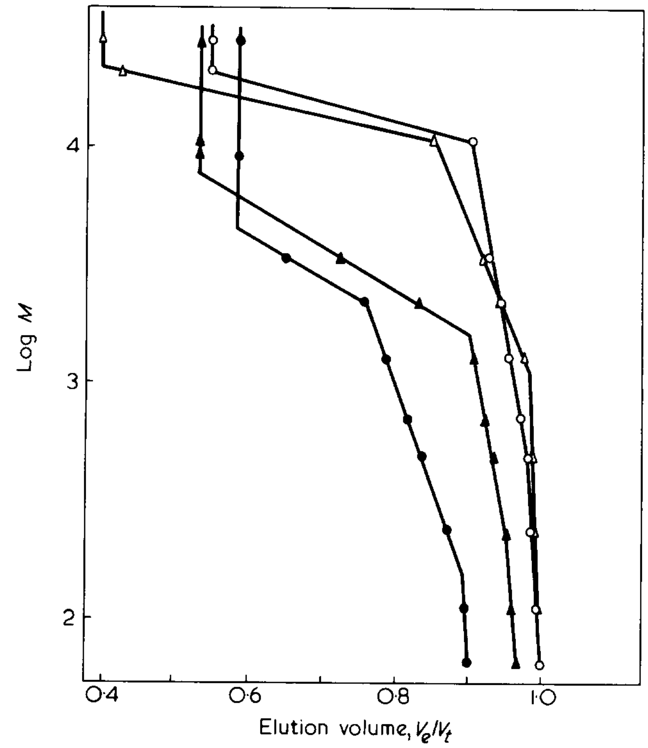

Figure 3 Calibration curves for A-type gels: ▲, A-1; △, A-3; ○, A-4; ●, A-6

density of the outer layer and that of the inner part of the gel.

Preparation conditions and properties of the B-type gels are shown in *Table 4*. Calibration curves for B and C-type gels are shown in *Figure 4*. B-1–B-4 gels were prepared from bead-shaped gels, which consisted of a PVA outer layer and a PVAc inner part, by crosslinking with epichlorohydrin followed by acetylation. As a result, these gels can be considered to be PVAc gels with a double layer structure consisting of a crosslinked outer layer and a non-crosslinked inner part. B-5–B-10 gels were crosslinked throughout, as the gels were prepared by copolymerization of PVAc and BDVE. The α values of the gels depended upon the thickness ratio in spite of a change in amount of crosslinking agent, epichlorohydrin, for the outer layer. The smaller the thickness ratios, the smaller are the α values. The difference in α value between B-2 and B-3 gels was caused by the amount of crosslinking agent, for the outer layer, epichlorohydrin. The larger the amount of epichlorohydrin used, the smaller were the values for M_{lim} and α. The α value of B-5 gel was 3.9; this large value was caused by a large thickness ratio of 1. B-6, B-7 and B-8 gels had small α values, which were caused by small BDVE contents as well as small thickness ratios. A difference of α value between B-6 and B-7 gels was caused by the amount of crosslinking agent, epichlorohydrin, in the outer layer. Large α values of B-9 and B-10 gels were mainly caused by large contents of BDVE.

Preparation conditions and properties of C-type gels are shown in *Table 5*. A result of X-ray line analysis with Cl–Kα and S–Kα at the section of a C-type gel is shown in *Figure 5*. It is evident that chloromethylation proceeded homogeneously through the gel beads. It is assumed that chloromethyl ether penetrated into gel beads, because tetrachloroethane, which is soluble in chloromethyl ether and a swelling agent of S–DVB copolymer, was added to the reaction mixture. The sulphur was located in an outer layer of the bead, because crosslinking with sodium sulphide occurred at the surface of the chloromethylated copoly(S–DVB) in water. Therefore, the gel can be considered to be a double layered structure which consists of crosslinked outer layer and lightly crosslinked inner part. α values of C-1–C-4 gels, that were not treated with crosslinking agents containing sulphur, were large. It is clear that these gels did not have a double layer structure, whereas, C-5–C-12 gels had a double layer structure. The smaller the contents of DVB, the smaller are the values of α. A difference in α values between two gels,

Table 4 Poly(BDVE—VAc) gels with a double layer structure

Gel no.	BDVE (vol %) for total monomer	Thickness ratio, *r*	Amount* of ECH (ml)	Degree of acetylation (mol %)	Degree of swelling (ml/g)	Solvent regain [methanol (g/g)]	M_{lim}	α
B-1	0.0	0.084	1.80	100	4.3	1.3	3700	2.1
B-2	0.0	0.041	1.00	100	5.8	2.0	3400	1.4
B-3	0.0	0.041	3.10	100	4.8	1.2	740	1.2
B-4	0.0	0.014	1.80	100	8.4	1.6	3400	0.9
B-5	0.1	1.000	1.25	53	5.1	1.0	5000	3.9
B-6	0.1	0.047	2.50	93	5.0	1.3	4200	0.7
B-7	0.1	0.047	1.25	64	9.0	2.7	4800	0.8
B-8	0.1	0.021	0.63	68	9.9	3.0	5200	0.8
B-9	0.5	0.047	10.00	100	5.6	1.3	4600	1.0
B-10	1.5	0.047	10.00	100	3.5	0.7	3200	4.0

* Amounts of other reagents: polymer (18 g), 10 N NaOH (40ml), medium (kerosene 100ml)

Table 5 Poly(S—DVB) gels with a double layer structure

Gel no.	DVB content (vol %) for total monomer	Cl content (wt %) in chloromethylated copolymer	Sulphur* (g)	Reaction time (h)	S_d [wet (ml)/ dry (g)]	S_r[ethyl acetate (g) dry-gel (g)]	M_{lim}	α
C-1	1.65	23.9	0.0	0.0	4.1	2.3	5000	2.6
C-2	0.83	26.0	0.0	0.0	6.1	2.9	12 000	2.3
C-3	0.55	22.6	0.0	0.0	6.2	3.0	17 000	2.3
C-4	0.28	26.3	0.0	0.0	11.2	4.7	40 000	2.1
C-5	1.65	23.9	0.2	1.0	3.7	2.2	3900	2.0
C-6	0.83	26.0	0.2	1.0	5.0	2.6	9600	1.9
C-7	0.55	22.6	0.2	1.0	5.4	2.8	11 000	1.1
C-8	0.55	22.6	0.2	5.0	5.4	2.8	10 500	0.6
C-9	0.44	27.1	0.2	1.0	5.4	2.8	9600	0.8
C-10	0.44	27.1	0.2	5.0	4.9	2.7	7200	0.6
C-11	0.28	26.3	0.2	3.0	9.6	4.3	15 000	0.7
C-12	0.28	26.3	0.2	5.0	8.2	3.9	15 800	0.6

* Amount of other reagents: H_2O (100 ml), Na_2S (25 g), chloromethylated copolymer (3 g)

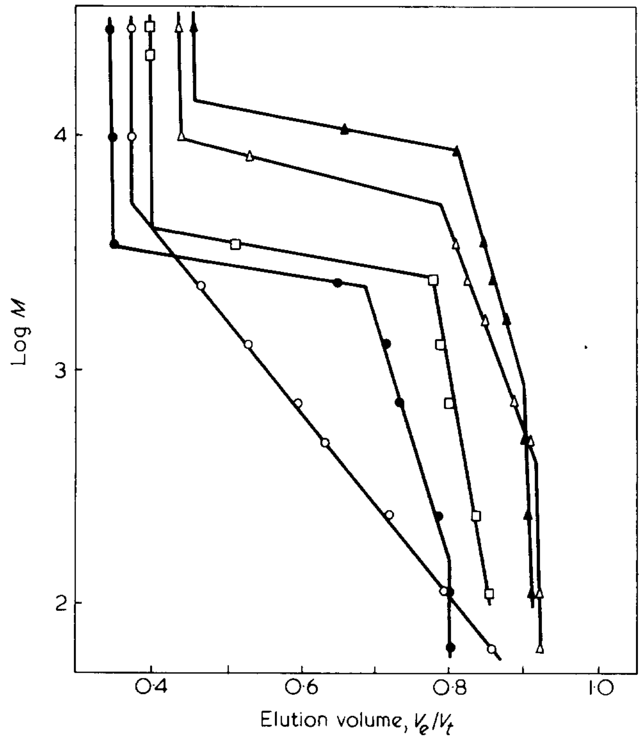

Figure 4 Calibration curves for B and C type gels: ▲, C-11; △, C-9; □, B-6; ○, B-5; ●, B-4

e.g., C-7 and C-8 gels, that contained the same amounts of DVB, was due to the reaction times with crosslinking agents. The longer the reaction times, the smaller are the values for M_{lim} and α.

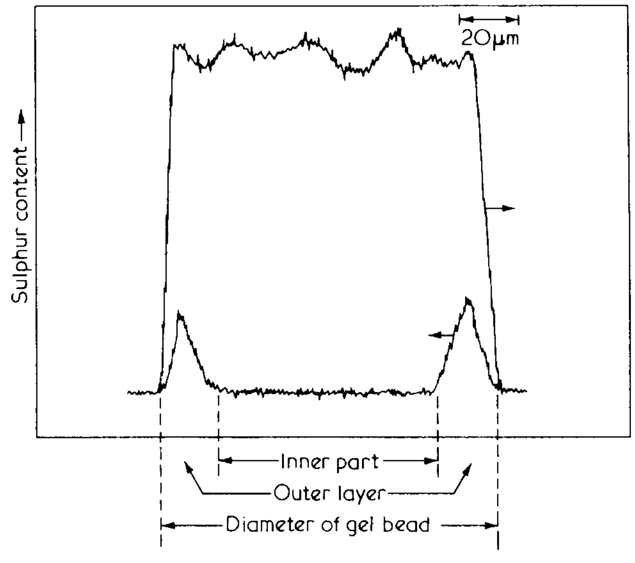

Figure 5 X-ray line analysis with S-Kα, Cl-Kα at the section of C-type gel bead

CONCLUSION

The characteristic separation obtained using hydrophobic gels with a double layer structure is caused by the structure of the gels, in which the ratio of the thickness of the outer layer to that of the inner part was small while the difference between crosslinking densities of both layers was sufficiently large.

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