Network of γ-irradiated poly(vinyl alcohol) beads

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The crosslinking of poly(vinyl alcohol) beads was performed by γ-ray irradiation. The maximum molecular size, M_{lim}, which can permeate through beads, was obtained by eluting poly(ethylene glycol) through a column packed with beads. The root-mean-square of the end-to-end distance $(\overline{r^2})^{1/2}$ and that of the hydrodynamic radius $(\overline{s^2})^{1/2}$ were also calculated. Meanwhile, the average size of the network of the beads, r_c, was estimated from the average molecular weight between crosslinkages, M_c, which was derived from the glass transition temperatures of crosslinked and non-crosslinked poly(vinyl alcohol) beads. r_c values of poly(vinyl alcohol) beads decreased as the total dose of γ-irradiation increased when dry poly(vinyl alcohol) beads were γ-irradiated, while the values were almost constant when poly(vinyl alcohol) beads swollen in water were γ-irradiated. Further, linear relations were obtained among r_c, $(\overline{r^2})^{1/2}$, and $(\overline{s^2})^{1/2}$ covering the wide range of total dose.

INTRODUCTION

A heterogeneous gel of a macroreticular structure and a homogeneous gel swollen by eluent are usually used as packing materials for gel permeation chromatography (g.p.c.). The former was investigated on the relationship between the pore size distribution and the elution behaviour of resolved substances. As to the latter, according to the previous paper[1] from this laboratory on hydrophobic crosslinked vinyl acetate–glycidyl methacrylate copolymer, a linear relation was found between the average size of the copolymer network obtained by dynamic viscoelastic measurements and the maximum size of permeable molecules measured by g.p.c. operation using dimethylformamide as an eluent. In the present paper, a network of poly(vinyl alcohol) (PVA) beads obtained by γ-irradiation at dry state or at swollen state in water has been investigated.

EXPERIMENTAL

Preparation of gel beads

Commercial vinyl acetate monomer was purified by distillation under atmospheric pressure at its boiling point of 72.5°–73.0°C. The bead-shaped poly(vinyl alcohol) gels were prepared from poly(vinyl acetate) beads by the previously reported saponification method[2].

γ-Irradiation beads

The bead-shaped poly(vinyl alcohol) gels, dried or swollen in water, were γ-irradiated in an open glass tube, as indicated in *Table 1*. ^{60}Co, 15 kCi and ^{60}Co, 45 kCi sources in The Japan Atomic Energy Research Institute were used for γ-irradiation.

Viscoelastic measurements

The previously reported M_c value was calculated from the equilibrium rubber elastic modulus, E_r, obtained by dynamic viscoelastic measurement[1]. A similar measurement was also carried out in the present work. After preparation of 0.3–0.5 mm thick poly(vinyl alcohol) sheet, the sheet sample was γ-irradiated. Dynamic viscoelastic measurements were carried out for the resulting poly(vinyl alcohol) sheet using the direct reading dynamic viscoelastometer (Tokyo–Bouldwin, Vibron Model DDV-1).

Glass transition temperature measurements

γ-Irradiated poly(vinyl alcohol) beads were acetylated with pyridine–acetic anhydride mixture. After drying the γ-irradiated poly(vinyl alcohol) beads, glass transition temperatures were measured using a dilatometer. The average molecular weight, M_c, between the crosslinkages was calculated by the following equation[3]:

$$T_g - T_g{}^0 = 3.9 \times 10^4/M_c$$

where T_g and $T_g{}^0$ are the glass transition temperatures of crosslinked and non-crosslinked polymers respectively. A network radius of crosslinked polymer, r_c, was derived from M_c[1].

Table 1 Conditions of γ-irradiation

Gel no.	Dose rate (R/h)	Total dose (R)	Temperature (°C)	Note
A–1	1.10×10^4	1.10×10^4	110	Dry
A–2	1.05×10^5	1.05×10^5	110	Dry
A–3	6.10×10^4	1.10×10^6	110	Dry
A–4	5.70×10^5	1.03×10^7	110	Dry
B–1	1.25×10^4	1.05×10^4	Room	In water
B–2	1.20×10^5	1.00×10^5	Room	In water
B–3	7.00×10^4	1.12×10^6	Room	In water
B–4	6.50×10^5	1.04×10^7	Room	In water

Table 2 Sample characteristics

No.	Material	M_n	M_w	Concentration (wt %)
E–1	EG	62		3
E–2	PEG	106		3
E–3	PEG	228		3
E–4	PEG	480		3
E–5	PEG	690		3
E–6	PEG	1280		3
E–7	PEG	2250		3
E–8	PEG	3400		3
E–9	PEG	9400		3
E–10	Dex T40	25 700	41 800	3
E–11	Dex 110	62 700	100 500	3
E–12	BDex	–	2 000 000	2

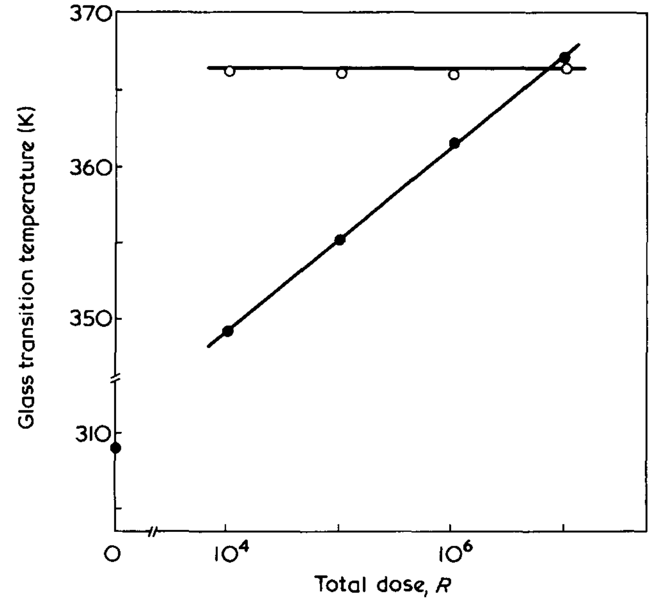

Figure 1 Plots of glass transition temperatures of PVAc gels *versus* total dose: ●, A-type gel; ○, B-type gel

G.p.c. operation

After γ-irradiated poly(vinyl alcohol) beads were allowed to swell in water at 60°C for 6 h, the g.p.c. operation was carried out using ion exchange water as an eluent.

A polymeric homologous series of ethylene glycol (PEG), dextrane (Dex), and blue dextrane (BDex) (Pharmacia Fine Chemicals, Sweden) were used as permeable substances as listed in *Table 2*. The excluded molecular weight, M_{lim}, was obtained from a calibration curve as shown in the previous paper[1].

RESULTS AND DISCUSSION

Average molecular weight between crosslinkages

The values of viscoelastic measurements in high temperature regions were not clear. The calculation of M_c from a equilibrium rubber elastic modulus would not be reasonable because these samples contain crystalline areas which are revealed by X-ray diffraction measurements. An attempt to calculate M_c by means of Flory's swelling theory was made, but an unjustifiable result was obtained from the calculation, since the measurement of temperature differences at swelling for crosslinked gel lead to M_c value differences. Therefore, M_c values were derived from the results of T_g measurements. T_g measurements of poly(vinyl alcohol) gels are not carried out accurately, because poly(vinyl alcohol) gels contain crystalline areas and are hygroscopic, while T_g measurements of poly(vinyl acetate) are carried out more accurately than those of poly(vinyl alcohol) because of its non-crystallinity and less hygroscopic nature. Therefore, the values of M_c were calculated from the results of T_g measurements of poly(vinyl acetate) gels prepared from poly(vinyl alcohol) by acetylation (*Figures 1* and *2*). The values of M_c decreased as the total dose of γ-irradiation increased when dry poly(vinyl alcohol) beads were γ-irradiated over the range of $10^4 \sim 10^7$ R at 110°C. Meanwhile the values of M_c are almost constant and lower than those of above mentioned dry poly(vinyl alcohol) beads, when poly(vinyl alcohol) beads swollen in water were γ-irradiated over the range of $10^4 \sim 10^7$ R. It is reasonable to assume that the value of M_c should decrease with the total doses but reach a constant value over the range of $10^4 \sim 10^7$R.

Extent of permeable molecules with maximum size

Figures 3 and *4* show the g.p.c. calibration curves for ethylene glycol and PEG with different molecular weights using γ-irradiated poly(vinyl alcohol) gels as a packing material and water as an eluent. It is found that these calibration curves have similar gradients. The maximum molecular weights of permeable substances, M_{lim}, were obtained from the calibration curves. The root-mean-square end-to-end distance $(\overline{r^2})^{1/2}$ and the root-mean-square hydrodynamic radius $(\overline{s^2})^{1/2}$ were estimated by the method of Ptitsyn and Eizner[4]:

$$[\eta] = \Phi(\epsilon)(\overline{r^2})^{1/2}/M = \Phi(\epsilon)(\overline{s^2})^{1/2}/(6)^{1/2}M$$

$$\Phi(\epsilon) = 2.86 \times 10^{23}(1 - 2.63\epsilon + 2.86\epsilon^2)$$

$$\alpha = (1 + 3\epsilon)/2$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight,

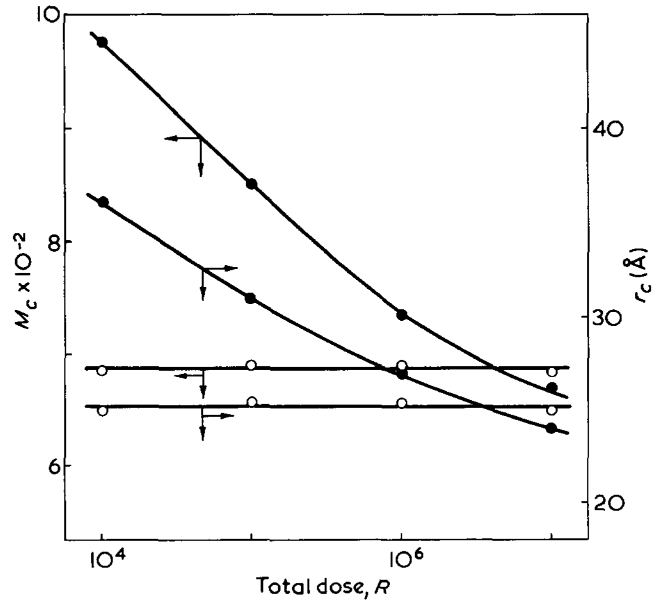

Figure 2 Plots of M_c and r_c *versus* total dose: ●, A-type gels; ○, B-type gels

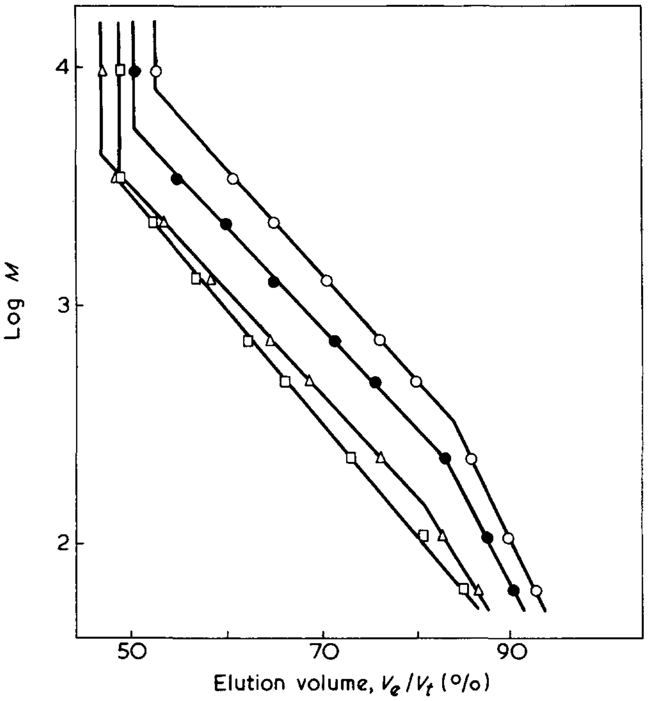

Figure 3 Calibration curves for the A-type gels: ○, A-1 gels; ●, A-2 gel; △, A-3 gel; □, A-4 gel

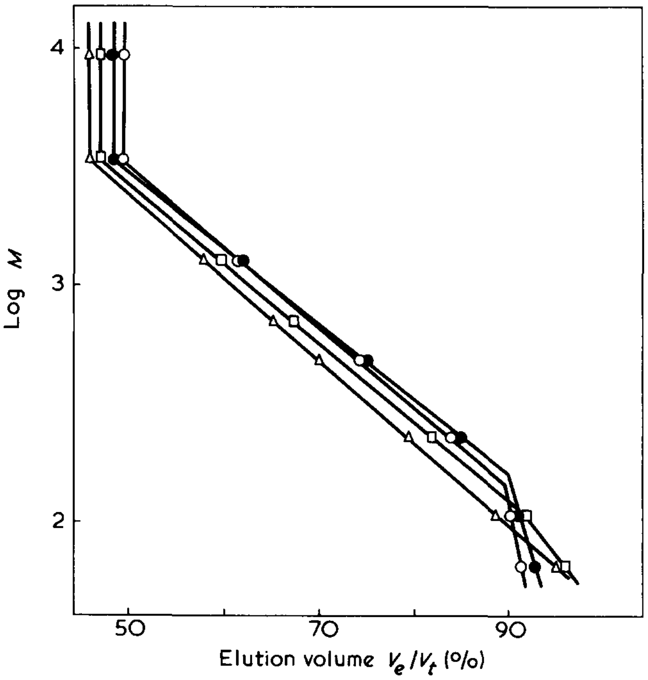

Figure 4 Calibration curves for the B-type gels: ○, B-1 gel; ●, B-2 gel; △, B-3 gel; □, B-4 gel

and α is the exponent of viscosity equation. The viscosity equation of PEG obtained at 30°C in water is as follows:

$$[\eta] = KM^{\alpha}$$

$$\alpha = 0.62, K = 6.61 \times 10^{-5}$$

Linear relations were found between $[\eta]$ and M over the total range of M_{lim}. Therefore the value of $\Phi(\epsilon)$ may be considered as constant. Using the gels that were γ-irradiated at a dry state, the A type gels, it is found that the values of $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ decrease as the total dose of γ-irradiation on the gels increases. Meanwhile, using the gels that were γ-irradiated at a swollen state in water, the B type gels, the values of $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ are almost constant in spite of the change of γ-irradiation dose (*Figure 5*). It is noteworthy that the values of r_c were closely approximate to those of $(\overline{s^2})^{1/2}$. Parallel relations are found among r_c, $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ over the total range of γ-irradiation dose (*Figure 6*). The plots of $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ *versus* r_c are shown in *Figure 7*. The linear relations among r_c, $(r^2)^{1/2}$ and $(s^2)^{1/2}$ are shown as follows:

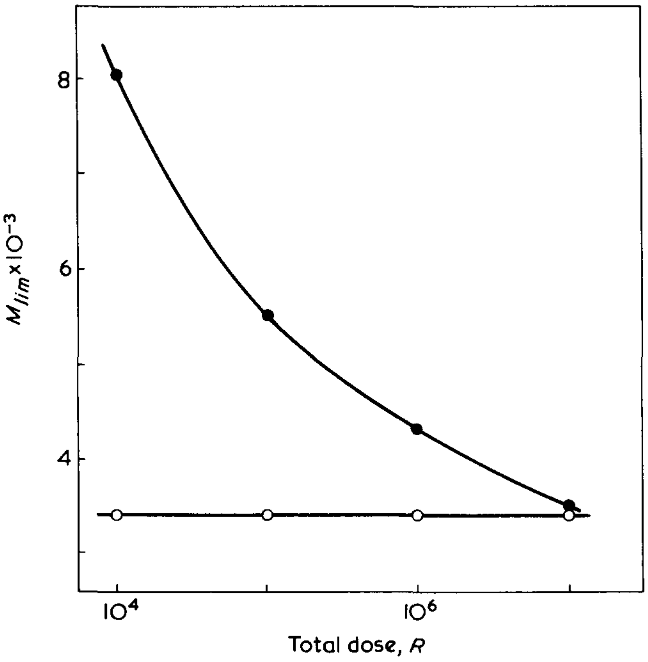

Figure 5 Plots of M_{lim} *versus* total dose: ●, A-type gels: ○, B-type gels

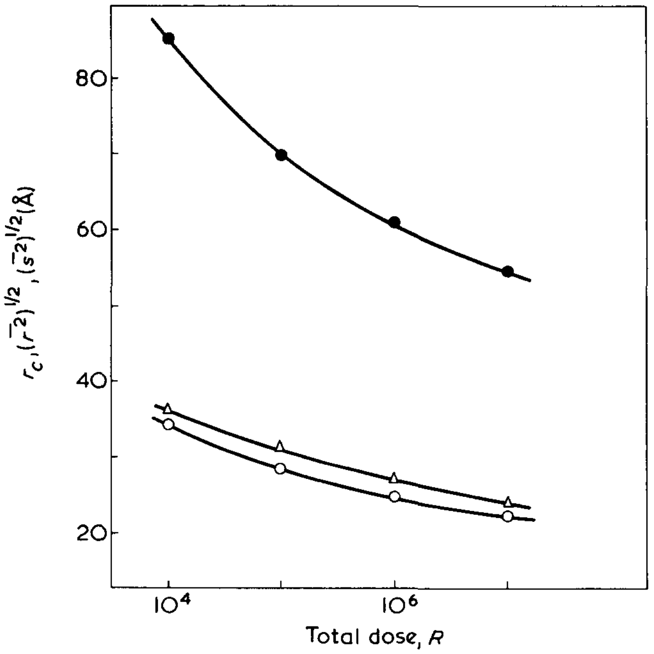

Figure 6 Plots of r_c, $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ *versus* total dose on the A-type gels: ●, $(\overline{r^2})^{1/2}$; ○, $(\overline{s^2})^{1/2}$; △, r_c

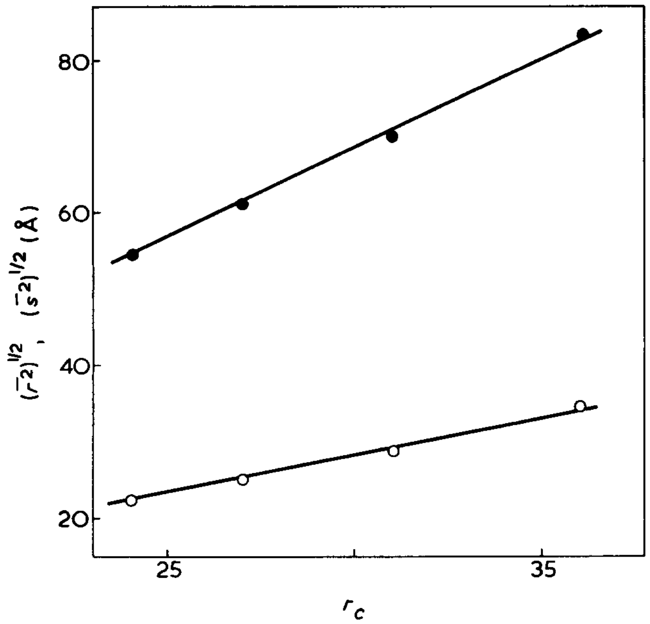

Figure 7 Plots of $(\overline{r^2})^{1/2}$ and $(\overline{s^2})^{1/2}$ *versus* r_c: ●, $(r^2)^{1/2}$; ○, $(s^2)^{1/2}$

$$r = 0.44(\overline{r^2})^{1/2} = 1.07(\overline{s^2})^{1/2}$$

The relations are very similar to the previous results[1] that were obtained using crosslinked vinyl acetate–glycidyl methacrylate copolymer as a gel and dimethylformamide as an eluent.

CONCLUSION

Average sizes of the network of a gel decrease as the total dose of γ-irradiation increases when dry poly(vinyl alcohol) beads were γ-irradiated, while the values are almost constant when poly(vinyl alcohol) beads swollen in water were γ-irradiated. Linear relations were found among the network size of the γ-irradiated poly(vinyl alcohol) gel and the root-mean-square end-to-end distance and the root-mean-square hydrodynamic radius of a molecule in water eluent when the gel was used as a g.p.c. packing material. Further, the average size of the network was closely approximate to the root-mean-square of hydrodynamic radius.

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