Excluded chain dimensions and network size in g.p.c.

Chuichi Hirayama, Mitsuaki Iida and Yoshiaki Motozato
Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami-machi, Kumamoto, 860, Japan

(*Received* 30 *May* 1980; *revised* 21 *February* 1981)

Attempts have been made to correlate the average network size of polystyrene, poly(methyl methacrylate), poly(methyl acrylate), poly(n-butyl acrylate) and poly(vinyl acetate) gels with the maximum size of the polymer molecule which can permeate the gels. The average size of the network structure (r_c) was estimated from the average molecular weight between crosslinkages (M_c) derived from the glass transition temperatures of the gels. The maximum molecular size which could permeate into the network was expressed as the root-mean-square end-to-end distance $[(\overline{r^2})^{1/2}]$ of the permeable substance with the molecular weight at exclusion limit (M_{lim}) obtained by gel permeation chromatography. Both r_c and $(\overline{r^2})^{1/2}$ decreased with increasing total dose of γ-irradiation or increasing amount of the crosslinking agent. Linear relations were also obtained between r_c and $(\overline{r^2})^{1/2}$ covering a wide range of total dose and amount of the crosslinking agent.

INTRODUCTION

A heterogeneous macroreticular gel or a homogeneous gel swollen by an eluent is usually used as packing material for gel permeation chromatography (g.p.c.). The former have been investigated to find the relation between pore size distribution and elution behaviour of separated mixtures. As to the latter, previous papers[1,2] on vinyl acetate–glycidyl methacrylate copolymers and poly(vinyl alcohol) gels found linear relations between the average size of the gel network obtained from rubber elastic modulus of glass transition temperature and the maximum size of the permeable molecule measured by g.p.c. But the ratios of network size to maximum size of permeable molecules were different from each other. In order to obtain more information about the relationship between network size and permeable molecular size, polystyrene, poly(methyl methacrylate), poly(methyl acrylate), poly(n-butyl acrylate) and poly(vinyl acetate) gels are reported here.

EXPERIMENTAL

Synthesis of polystyrene (PSt) gel beads

Styrene monomer was purified by vacuum distillation at 48 ~ 49°C/23 mmHg. Bead-shaped PSt gels were prepared from solutions containing various amounts of divinylbenzene (DVB) as crosslinking agent and 2 wt % benzoyl peroxide (BPO) as initiator in 20 ml styrene monomer, by suspension in 200 ml of a 2 wt % gelatin aqueous solution under constant stirring at 60°C for 24 h. The PSt gel beads obtained were washed with hot water to remove the gelatin.

Synthesis of poly(methyl methacrylate) (PMMA) gel beads

Commercial methyl methacrylate monomer was purified by vacuum distillation. Bead-shaped PMMA gels were prepared from solutions containing various amounts of DVB as crosslinking agent and 2 wt % BPO as initiator in 10 ml purified methyl methacrylate monomer by suspension in 200 ml of 2 wt % gelatin–1 wt % Na_2HPO_4 aqueous solution under constant stirring at 60°C for 24 h. The PMMA gel beads obtained were washed with hot water to remove the gelatin.

Synthesis of poly(vinyl acetate) (PVAc) gel beads

Commercial vinyl acetate monomer was purified by distillation under atmospheric pressure at 72.5 ~ 73.0°C. Three kinds of beads were prepared as follows.

Slightly branched PVAc beads (brl-PVAc). PVAc beads were prepared from solutions containing 1 wt % BPO in 300 ml purified vinyl acetate monomer, by suspension in 700 ml of 1 wt % gelatin aqueous solution under constant stirring at 60°C for 7 h. The brl-PVAc beads obtained were washed with warm water to remove the gelatin.

Linear PVAc beads (l-PVAc). Poly(vinyl alcohol), (PVA) was prepared from a solution containing 20 g of the above PVAc beads in 400 ml of methanol, by dropping 20 ml of 5NNaOH aqueous solution into the PVAc methanolic solution under constant stirring for 1 h at room temperature. The PVA was washed with methanol, dried *in vacuo* for 2 days and then acetylated with pyridine and acetic anhydride at 90°C for 24 h[3]. l-PVAc beads were prepared from solutions containing 10 g of acetylated PVA in 100 ml CH_2Cl_2, by suspension in 1000 ml of 3 wt % gelatin aqueous solution under constant stirring at 30°C for 12 h.

Branched PVAc beads (br2-PVAc). The monomer solution, which contained 0.02 wt % BPO in 75 ml of purified vinyl acetate, was polymerized under reflux at 70°C for 48 h. The product was purified by reprecipitation of a benzene solution into petroleum ether. From the purified bulk PVAc, the bead-shaped br2-PVAc was prepared in a same manner as l-PVAc.

Crosslinking of all PVAc beads was by γ-irradiation in water at room temperature. Gel beads obtained were

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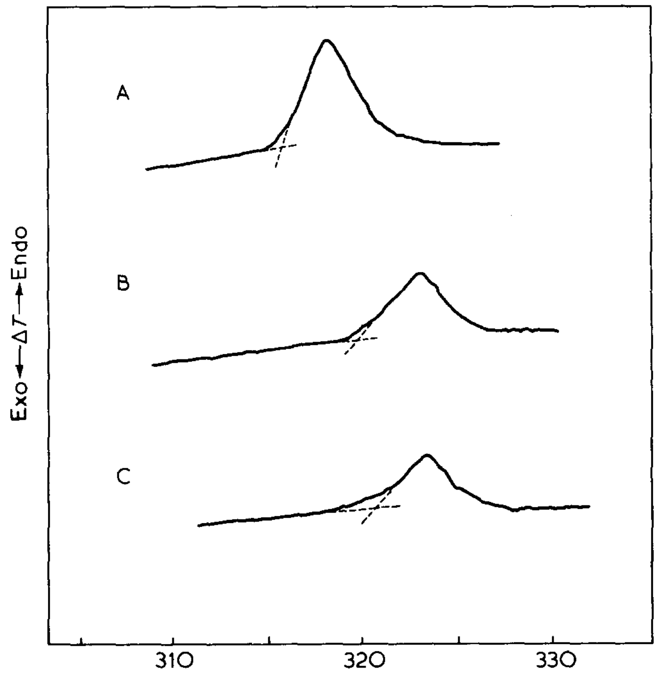

Figure 1 D.s.c. thermograms for PVAc beads (A) and γ-ray-irradiated PVAc beads (B, C). The total dose of γ-ray-irradiation – (A), 0 R; (B), 3.2 x 10^7 R; (C), 1.0 x 10^8 R

washed with methanol to remove the non-crosslinked polymer. ^{60}Co [15 kCi] and ^{60}Co [45 kCi] sources in The Japan Atomic Energy Research Institute were used for γ-irradiation.

Synthesis of poly(methyl acrylate) (PMeA) gel beads

PMeA gel beads were prepared from solutions containing 2 wt % BPO in 20 ml monomer purified by vacuum distillation, by suspension in 200 ml of 4 wt % gelatin, 15 wt % anhydrous Na_2SO_4 and 1 wt % Na_2HPO_4 aqueous solution at 60°C for 24 h, followed by crosslinking by γ-irradiation in a similar manner as above.

Synthesis of poly(n-butyl acrylate) (PBuA) gel beads

Purification of n-butyl acrylate monomer and γ-irradiation of the PBuA beads obtained by suspension polymerization were carried out in the same manner as for PMeA gel beads.

Glass transition temperature measurements

Gel beads were dried *in vacuo* for 7 days, and their glass transition temperatures measured by differential scanning calorimetry (Shimazu, DSC-20).

G.p.c. operation

After swelling PSt, PMMA, PMeA and PBuA beads in toluene, g.p.c. was carried out with distilled toluene as an eluent. A homologous series of polystyrenes were used as permeable substances. For PVAc gels, g.p.c. was carried out using distilled methanol as an eluent, and a homologous series of poly(ethylene glycols) as permeable substances. The molecular weight at the exclusion limit ($M_{\rm lim}$) was obtained from a calibration curve as shown previously[1].

RESULTS AND DISCUSSION

Average size of the network

The average molecular weight between the crosslinkages (M_c) was calculated by the following equation[4–6]:

$$T_g - T_g^0 = 3.90 \times 10^4 / M_c \qquad (1)$$

where T_g and T_g^0 are the glass transition temperatures of crosslinked and non-crosslinked polymer, respectively. *Figure 1* shows some d.s.c. thermograms for γ-irradiated PVAc beads. Then the number of bonds in the chain between the crosslinkages (n) can be obtained from the molecular weight of the repeating unit (m) and M_c:

$$M_c = n(m/2) \qquad (2)$$

Consequently, the mean square end-to-end distance of the unperturbed chain between the crosslinkages $[(\overline{r^2})_0^{1/2}]$ was estimated from the equation[7]:

$$(\overline{r^2})_0 = C_\infty n l^2 \qquad (3)$$

where l is the bond length, 1.54 Å, and C_∞ is the characteristic ratio, i.e. PSt 10.6, PMMA 9.0, PMeA 8.4, PBuA 9.0 and PVAc 9.4, taken from reference 8. The network structure made up of the chain between the crosslinkages was swollen in a solvent. Therefore the average size of the network structure (r_c) is expressed as:

$$r_c = (\overline{r^2})_0^{1/2} q^{1/3} \qquad (4)$$

where q is the degree of swelling.

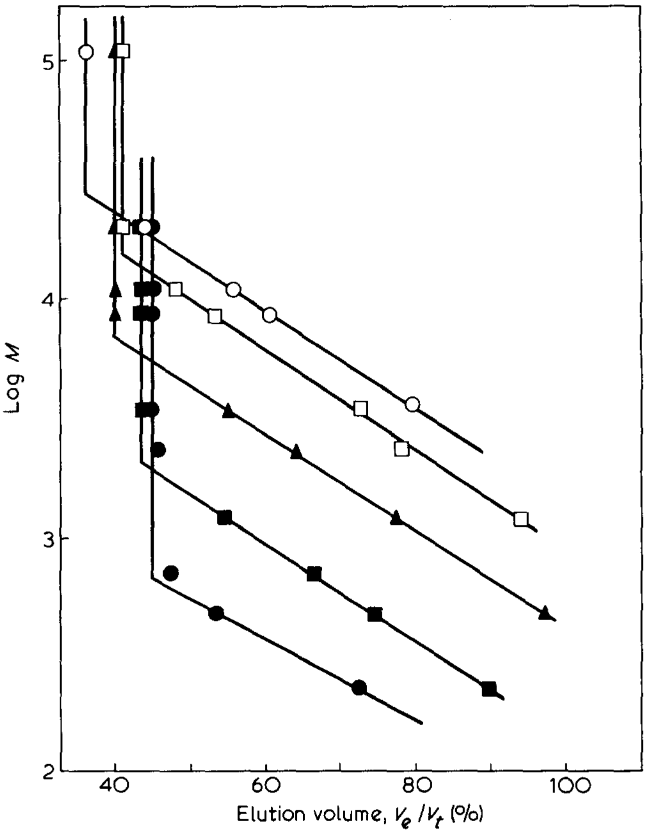

Figure 2 Calibration curves for PSt gels. Mol percent of DVB in total monomer – ○, 0.40; □, 0.48; ▲, 0.80; ■, 2.43; ●, 8.30

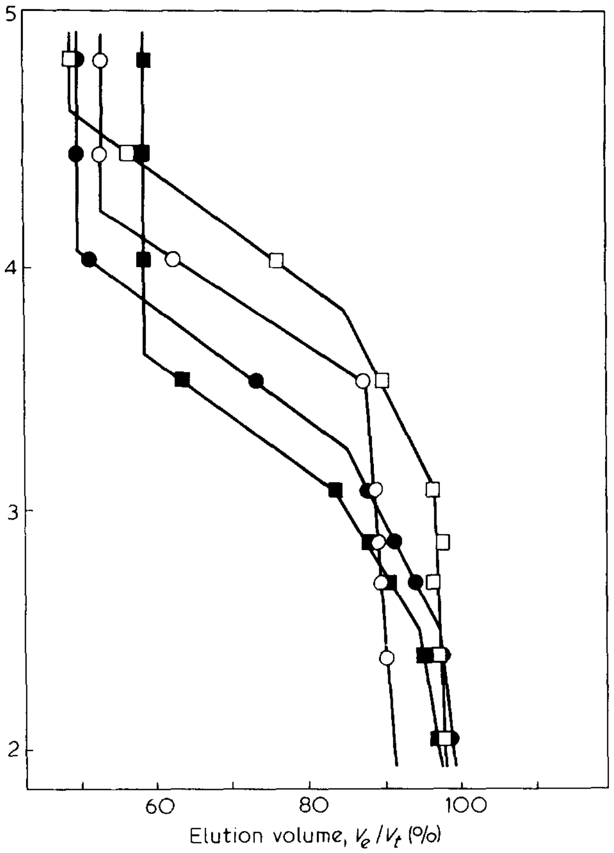

Figure 3 Calibration curves for 1-PVAc gels. The total dose of γ-ray-irradiation – □, 1.0×10^7R; ○, 3.2×10^7R; ●, 5.2×10^7R; ■, 1.0×10^8R

Extent of permeable molecules with maximum size

Figure 2 shows the g.p.c. calibration curves for polystyrene standards using PSt gels as packing material and toluene as an eluent. *Figure 3* shows the g.p.c. calibration curves for poly(ethylene glycol) series using PVAc gels as packing material and methanol as an eluent. The maximum molecular weight of permeable substances, i.e. the molecular weight at exclusion limit (M_{lim}), was obtained from these calibration curves. So the extent of the permeable molecules with maximum size was expressed as the root-mean-square end-to-end distance $[(\overline{r^2})^{1/2}]$, estimated by the method of Ptitsyn and Eizner[9]:

$$[\eta] = \Phi(\overline{r^2})^{3/2}/M$$
$$\Phi = 2.86 \times 10^{23}(2 - 2.63E + 2.86E^2)$$
$$a = (1 + 3E)/2$$
$$[\eta] = KM^a$$

polystyrene–toluene, 25°C: $K = 9.20 \times 10^{-3}$; $a = 0.72$
poly(ethylene glycol)–methanol, 25°C: $K = 8.52 \times 10^{-2}$; $a = 0.57$

where $[\eta]$ is intrinsic viscosity, M is molecular weight, and the values of K and a in the viscosity equation are quoted from references[10,11].

r_c, $(\overline{r^2})^{1/2}$ of PSt and PMMA gels

The glass transition temperatures (T_g) and the degree of swelling (q) of PSt and PMMA gels are shown in *Figure 4*. Because of increase of crosslinking density, T_g increases and q decreases. *Figure 5* shows the average molecular weight between crosslinkages (M_c) derived from T_g and also shows the molecular weight at exclusion limit (M_{lim}) obtained from the calibration curve. Further, r_c derived from M_c and $(\overline{r^2})^{1/2}$ from M_{lim} are shown in *Figure 6*. As the amount of crosslinking agent increases, r_c and $(\overline{r^2})^{1/2}$ both decrease. As shown in *Figures 4*, *5*, and *6*, the crosslinking density of PMMA gel is larger than that of PSt gel at the same mole fraction of crosslinking agent. The reactivity ratios in copolymerization of styrene $[M_1]$ and DVB $[M_2]$ are $r_1 = 0.65$, $r_2 = 0.60$ and those of methyl methacrylate $[M_1]$ and DVB $[M_2]$ are $r_1 = 0.09$, $r_2 = 0.10$, respectively. Comparing these reactivity ratios, it is supposed that the content of crosslinking agent in PMMA gel is larger than in PSt gel, even if the mole fraction of DVB in the monomer mixture is the same. For this reason, r_c and $(\overline{r^2})^{1/2}$ of PMMA gel are probably smaller than for PSt gel.

Figure 6 shows similar relations between r_c and $(\overline{r^2})^{1/2}$. It is found from *Figure 9*, which shows the relationship between r_c and $(\overline{r^2})^{1/2}$, that $(\overline{r^2})^{1/2}$ is proportional to r_c for both PSt and PMMA gels. The difference in the slopes for PSt and PMMA gels will be explained below.

r_c, $(\overline{r^2})^{1/2}$ of PVAc, PMeA and PBuA gels

Figure 7 shows the relationship between γ-irradiation total dose and r_c, $(\overline{r^2})^{1/2}$ of 1-PVAc, PMeA and PBuA gels. Values of r_c and $(\overline{r^2})^{1/2}$ decrease as the total dose of γ-irradiation increases. Furthermore, parallel relations between r_c and $(\overline{r^2})^{1/2}$ are exhibited by all three kinds of gel.

As shown in *Figure 7*, the degree of crosslinking by γ-irradiation decreases in the order PMeA, PBuA and PVAc. The reason why the degree of crosslinking in PVAc is the smallest is that the temperature of γ-irradiation is

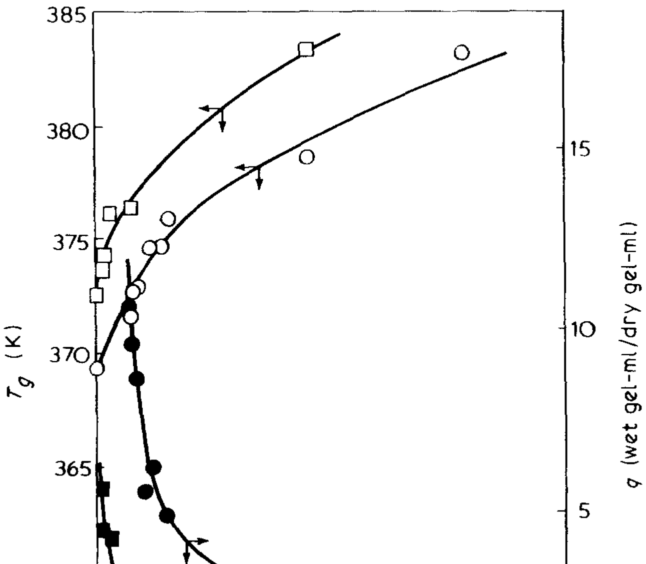

Figure 4 Effect of DVB content in total monomer on T_g and q: ○, T_g of PSt gels; ●, q of PSt gels; □, T_g of PMMA gels; ■, q of PMMA gels

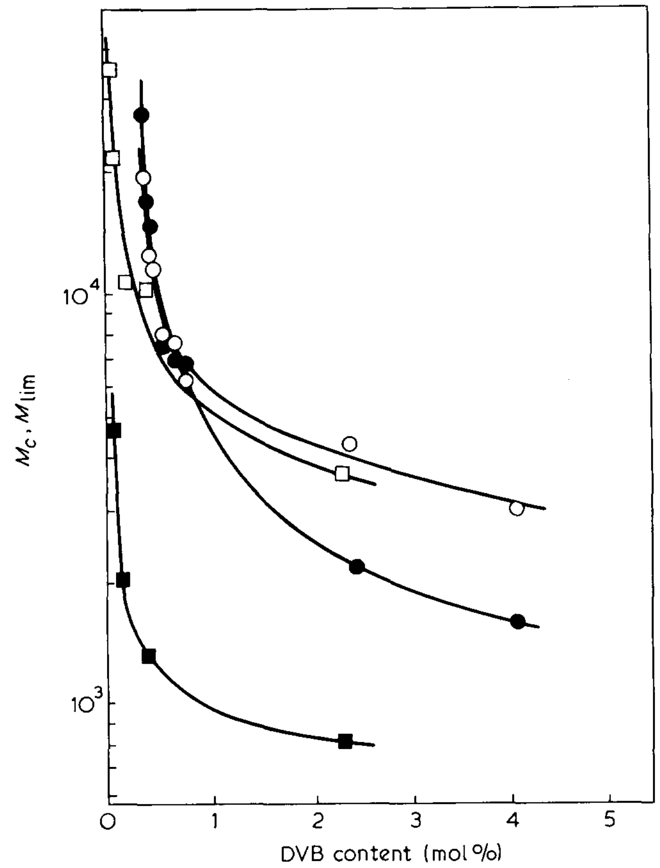

Figure 5 Effect of DVB content in total monomer on M_c and $M_{\rm lim}$: ○, M_c of PSt gels; ●, $M_{\rm lim}$ of PSt gels; □, M_c of PMMA gels; ■, $M_{\rm lim}$ of PMMA gels

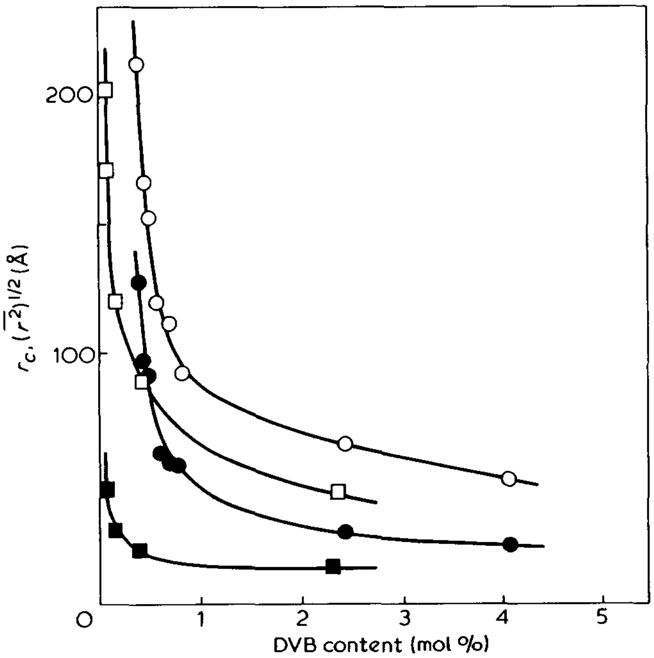

Figure 6 Effect of DVB content in total monomer on r_c and $(\overline{r^2})^{1/2}$: ○, r_c of PSt gels; ●, $(\overline{r^2})^{1/2}$ of PSt gels; □, r_c of PMMA gels; ■, $(\overline{r^2})^{1/2}$ of PMMA gels

lower than the glass transition temperature in PVAc and higher than the glass transition temperatures in PMeA and PBuA. At temperatures higher than the glass transition temperature, the polymer chain segments can move so easily that the crosslinking reaction by coupling of radicals is easy. For PBuA, the crosslinking reaction is more difficult than for PMeA because of the steric hindrance of the n-butyl group. Thus, the degree of crosslinking in PBuA is smaller than in PMeA.

The relationship between r_c and $(\overline{r^2})^{1/2}$ for PVAc gels is shown in *Figure 8*. PVAc polymerized by the usual method is known to be branched due to chain transfer reactions. Branches can be broken by saponification producing a linear PVA. Thus, the degree of polymerization of branched PVAc (br-PVAc) is larger than that of the saponified PVA. So, the ratio of the degree of polymerization of PVAc to that for saponified PVA can be used to express the degree of branching (*Figure 8*). In the case of linear PVAc (l-PVAc) this ratio equals 1 but increases as the degree of branching of br-PVAc increases. It is found from *Figure 8* that the larger the degree of

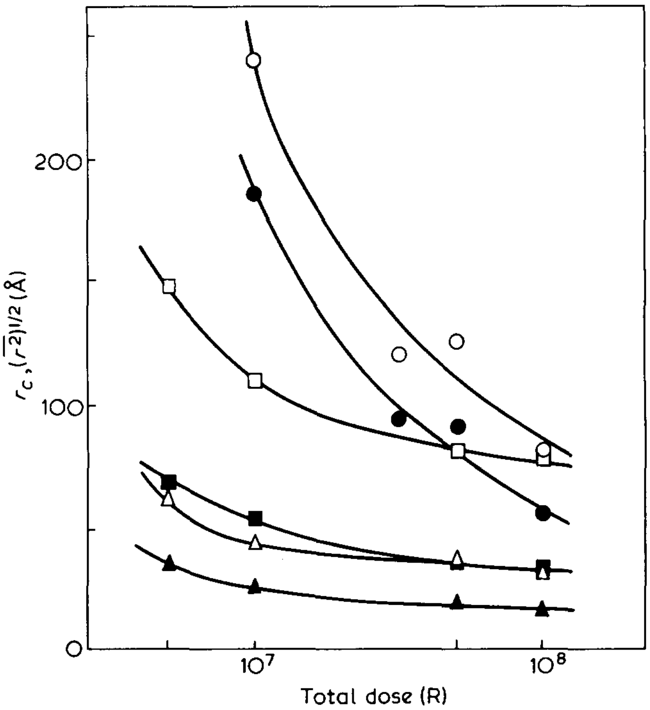

Figure 7 Effect of total dose of γ-ray-irradiation on r_c and $(\overline{r^2})^{1/2}$: ○, r_c of 1-PVAc gels; ●, $(\overline{r^2})^{1/2}$ of 1-PVAc gels; □, r_c of PBuA gels; ■, $(\overline{r^2})^{1/2}$ of PBuA gels; △, r_c of PMeA gels; ▲, $(\overline{r^2})^{1/2}$ of PMeA gels

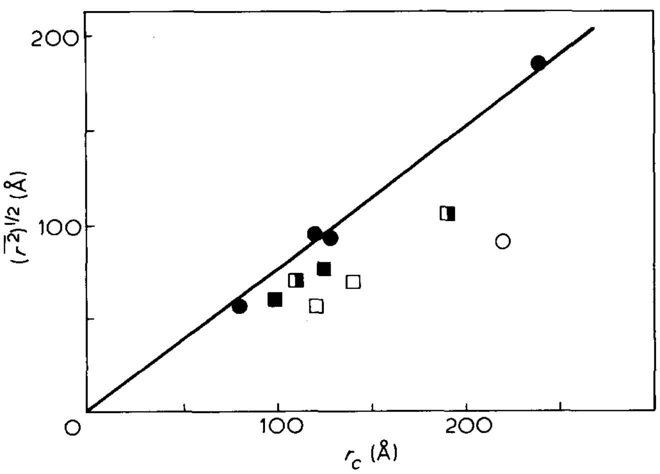

Figure 8 Relationship between r_c and $(\overline{r^2})^{1/2}$ for PVAc gels. The ratio of the degree of polymerization of PVAc to that of the saponified PVA – ●, 1.04; ■, 2.23; ◧, 3.39; □, 5.50; ○, 7.44

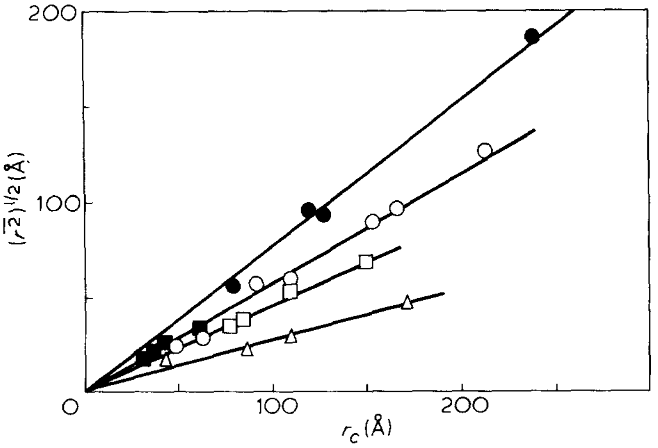

Figure 9 Relationship between r_c and $(\overline{r^2})^{1/2}$ for various gels: ○, PSt gels; △, PMMA gels; ●, 1-PVAc gels; ■, PMeA gels; □, PBuA gels

branching, the smaller the value of $(\overline{r^2})^{1/2}$ at the same value of r_c. Differences may be attributed to the steric hindrance caused by branches of PVAc.

As shown in *Figure 9*, for l-PVAc, PMeA and PBuA gels, $(\overline{r^2})^{1/2}$ is found to be proportional to r_c. Plots of r_c against $(\overline{r^2})^{1/2}$ for various gels were at first expected to be a single straight line. But according to the experimental results the relationships in *Figure 9* hold. The reason for these deviations may be explained since values of r_c were derived only from T_g data taken on gel matrices, while $(\overline{r^2})^{1/2}$ was derived from g.p.c., and included the interaction of gel matrices with permeable substances.

CONCLUSION

Linear relations were found between network size of PSt, PMMA, PVAc, PMeA and PBuA gels and the maximum size of molecule which could permeate into these gels in g.p.c. The ratios of the size of the permeable molecules to the size of the gel network differ and differences can be attributed to steric hindrance of the permeable molecules by the gel matrices.

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