Small-angle neutron scattering from poly(vinyl alcohol)-borate gels

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The structure of poly(vinyl alcohol) (PVA) aqueous gels containing borate ions (i.e. PVA-borate gels) was investigated with small-angle neutron scattering. The correlation length ξ, a measure of the spatial length of concentration fluctuation, was estimated from a generalized Zimm plot for fractals having the fractal dimension of D. The variation of ξ with temperature showed a gel-to-sol transition. The correlation length remained constant in the gel state and decreased steeply with increasing temperature in the sol state. Even at the highest temperature of observation (95°C) ξ was a few times greater than the radius of gyration of the PVA molecules, which indicates presence of PVA clusters in the sol state. The scattered intensity functions for the gels at different temperatures could be superimposed by employing reduced variables, $I(q)/c\xi^3$ and ξq, where c and q are the monomer concentration and the magnitude of the scattering vector, respectively. This indicates that the system is composed of domains of PVA clusters filling the space. The fractal dimension of PVA inside the domain is 2.6 to 2.8. This suggests that PVA chains in the domain are packed more densely than percolation clusters. In the sol state, the system is described as an ensemble of polydisperse clusters of $D \simeq 2.2$.

(Keywords: poly(vinyl alcohol); gel; small-angle neutron scattering; sol–gel transition; borate ion; fractal)

INTRODUCTION

Structural investigations of gels have been greatly advanced due to developments of experimental techniques, such as quasi-elastic light scattering[1,2] and small-angle neutron scattering (SANS)[3–8], and theoretical progress, such as scaling concepts[9] and fractals[10–15]. There are two streams in the theoretical development of polymer gels, i.e. classical and percolation theories. The former, which originated from the pioneering work of Flory[16] and Stockmayer[17], describes gels as a combination of points and lines (Bethe lattice) while the latter describes them as a body containing spatial defects. Since they predict different critical exponents on gelation from each other, experimental verification is one of the current topics of interest about the structural investigation of gels. For example, Adam *et al.*[18] showed that chemically crosslinked polyurethane gels by polycondensation have the same critical exponents as those predicted by the percolation theory. These techniques and theories now permit structural investigation of complex systems like physical gels.

However, most of the studies were made on diluted solutions of finite clusters just below the gelation threshold. In this case, self-similarity was often found and the fractal dimension was evaluated from the slope of the plot of log $I(q)$ *versus* log q, where $I(q)$ is the scattered intensity at the magnitude of the scattering vector q. Polymer networks at swelling equilibrium were also studied so as to envisage the chain conformation from the microscopic point of view. Structural investigation of a mixture of gel and sol, such as gels in a reactor bath or thermo-reversible gels, have not been extensively made. Martin and Wilcoxon[8] recently discussed that there exist two types of correlation in gels: the connectivity correlation and spatial correlation. At the gelation threshold the connectivity correlation diverges, whereas the spatial correlation remains finite. This can be observed as a physical cut-off at low-q region (or large-r region, where r is the distance). This may be the case for poly(vinyl alcohol)-borate complex, as will be reported below.

Poly(vinyl alcohol) gels behave as chemical or physical gels due to hydrogen bonding and/or chemical reaction of hydroxy groups. The hydrogen bonding plays an important role in the crystallization of PVA, even in solution, resulting in gelation. Pioneering work by Prins *et al.*[1,2] revealed that PVA gels were formed via liquid–liquid phase separation followed by crystallization of PVA chains. Komatsu *et al.*[19] studied the kinetics of spinodal decomposition and gelation of PVA aqueous solution. They found that the wavelength of the concentration fluctuation was of the order of a few tens of micrometres.

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Table 1 Qualitative comparison between the hydrogels and alkaline gels prepared from PVA aqueous solution

	Hydrogel	Alkaline gel
Preparation	Quenching of PVA aqueous solution	By adding (a) trace of $B(OH)_3$ and NaOH or (b) conc. NaOH
Mechanical properties	Non-rubber-like	Rubber-like
Optical properties	Turbid	Clear
Gel–sol transition	Non-reversible (hysteresis)	Reversible
Crosslinker	Microcrystallites	Borate-aided crosslinks[23]

Under alkaline conditions, some inorganic ions, e.g. borate ions[20] and cupric ions[21], react with PVA hydroxy groups and form crosslinks. Microscopic structures of PVA gels of this kind, hereafter referred to as alkaline gels, are not well understood. *Table 1* shows a qualitative comparison between the two types of gels, These gels differ in mechanical and optical properties. Hydrogels, i.e. PVA aqueous gels without borate ions, are relatively brittle and less clear in comparison with alkaline gels, depending on the history of the gel. This is due to crystallization of PVA in hydrogels. The sol–gel transition of alkaline gels is reversible and reproducible with respect to temperature, as reported elsewhere[22].

In previous papers, the present authors proposed a possible mechanism[23] for the crosslinking between PVA chains in the presence of borate ions and found a master relationship[22] on the sol–gel transition temperature, PVA and borate concentrations, and the degree of polymerization of PVA. Structures of PVA physical gels, i.e. PVA-hydrogels, were also investigated by SANS[24], where a two-phase model composed of aggregate-rich and -poor phases was proposed. We report here the temperature and concentration dependence of the scattered intensity function based on a generalized Zimm equation for a system having a fractal dimension D, and try to elucidate the structure of alkaline gels. It should be stressed here that the objective is not to verify whether the percolation theory or classical theory of gelation describes the gelation process of PVA, but to elucidate the structure of PVA-borate gels by observing an apparent fractal dimension.

THEORETICAL BACKGROUND

Consider first the asymptotic behaviour of the scattered intensity function, $S(q)$, for the gel's phase, where q is the magnitude of the scattering vector. Consider a general situation where the system consists of a compact arrangement of uncorrelated domains of size ξ. Let the monomer density correlation within each domain decay with distance r according to r^{D-d} ($r < \xi$), where D is the fractal dimension inside the domain and d is the space dimension. For this case, the scattered intensity for the system is proportional to

$$S(q) \sim c \int \mathrm{d}^d \boldsymbol{r} \exp[\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}](\xi/r)^{d-D}\exp[-r/\xi]$$
$$\sim c\xi^{d-D}q^{-D}f(\xi q) \tag{1}$$

where c is the monomer concentration and the scaling function $f(x)$ has the asymptotic limits

$$f(x) \sim \begin{cases} x^D\left\{1 - \dfrac{D(D+1)}{2d}x^2 + \cdots\right\} & x \ll 1 \\ 1 & x \gg 1 \end{cases} \tag{2}$$

Therefore we obtain the asymptotic behaviour of $S(q)$ in three dimensions ($d = 3$) as

$$S(q) \sim \begin{cases} c\xi^3\left\{1 - \dfrac{D(D+1)}{6}\xi^2 q^2 + \cdots\right\} & \xi q \ll 1 \\ c\xi^{3-D}q^{-D} & \xi q \gg 1 \end{cases} \tag{3}$$

Thus an approximate interpolation formula can be written for $S(q)$:

$$S(q) \sim \frac{c\xi^3}{\left\{1 + \dfrac{(D+1)}{3}\xi^2 q^2\right\}^{D/2}} \tag{4}$$

Next consider the sol state where the clusters are polydisperse. For a single cluster of s monomers with radius of gyration R_s and fractal dimension D, ($R_s^D \sim s$), the structure factor is given by

$$S_s(q) \sim c \int \mathrm{d}^d\boldsymbol{r} \exp[\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}]r^{D-d}g(r/R_s) \tag{5}$$

where $r^{D-d}g(r/R_s)$ is the monomer density correlation function. Therefore

$$S_s(q) \sim \begin{cases} cs\{1 + O(R_s^2 q^2)\} & R_s q \ll 1 \\ cq^{-D} & R_s q \gg 1 \end{cases} \tag{6}$$

For a collection of clusters where the number of clusters of monomers s is ruled by the distribution $s^{1-\tau}h(s^\sigma(T - T_{\mathrm{gel}}))$, the structure factor becomes

$$S(q) \sim c \int \mathrm{d}s\, s^{1-\tau}h(s^\sigma(T - T_{\mathrm{gel}}))S_s(q) \tag{7}$$

where h is a scaling function. The symbols σ and τ are exponents describing the polydispersity and $T - T_{\mathrm{gel}}$ is the temperature relative to the sol–gel transition temperature. As shown by Martin and Ackerson[13] and Bouchaud *et al.*[6], it transpires that

$$S(q) \sim cq^{-D(3-\tau)}h(\xi q) \tag{8}$$

where

$$h(x) \sim \begin{cases} x^{D(3-\tau)}(1 - x^2 + \cdots) & x \ll 1 \\ 1 & x \gg 1 \end{cases} \tag{9}$$

Here ξ is defined to be $(T - T_{\mathrm{gel}})^{-1/\sigma D}$. As argued by Bouchaud *et al.*[6], if there exists a regime of q such that $qR_{\mathrm{m}} \gg 1$, where R_{m} is the radius of gyration of the smallest cluster in the system, then $S(q)$ is independent of the distribution, i.e.

$$S(q) \sim cq^{-D} \qquad R_{\mathrm{m}}q \gg 1 \tag{10}$$

Therefore $S(q)$ is given by

$$S(q) \sim cq^{-D(3-\tau)}\mathscr{S}(R_{\mathrm{m}}q) \tag{10a}$$

with

$$\mathscr{S}(R_{\mathrm{m}}q) \sim \begin{cases} 1 & R_{\mathrm{m}}q \ll 1 \\ (R_{\mathrm{m}}q)^{D(2-\tau)} & R_{\mathrm{m}}q \gg 1 \end{cases} \tag{11}$$

Therefore, by combining the results of equations (8)–(11):

$$S(q) \sim \begin{cases} c\xi^{D(3-\tau)} & \xi q \ll 1 \\ cR_{\mathrm{m}}^{D(2-\tau)}q^{-D} & R_{\mathrm{m}}q \gg 1 \end{cases} \tag{12}$$

Table 2 Sample characteristics

Sample code	PVA (wt%)	$B(OH)_3$ (10^{-2} M)	NaOH (10^{-1} N)
A4 (A4-aged)	12.5	1.67	1.51
A6 (A6-aged)	16.7	1.67	1.51

EXPERIMENTAL

Material

Re-saponified PVA powders, having a degree of polymerization $P = 120$, were kindly supplied by Unitika Chemical Co. Ltd., Japan. The details of the microstructure of PVA were reported in the previous papers[22,24].

Sample preparation

In order to avoid inhomogeneity and local gelation and/or coagulation, deuterated water solutions of PVA, boric acid and NaOH were prepared separately. Deuterated water solutions of PVA were prepared by dissolving PVA powder into deuterated water at *ca.* 90°C in a flask connected to a reflux condenser and by stirring for several hours. Sample solutions for SANS were prepared by mixing the prescribed amounts in the initial solutions. Solutions which instantly became gel on mixing were homogenized by heating above the sol–gel transition temperature. Two types of samples having different ageing time, as-prepared (A4 and A6) and aged for two months (A4-aged and A6-aged), were prepared in order to investigate the time evolution of gel structure. The initial concentrations of the solutions are listed in *Table 3*. The composition ratio of (PVA initial solution): 0.2 M $B(OH)_3$: 1.8 N NaOH was chosen so as to observe the gel–sol transition in the temperature range of SANS experiments, i.e. 20°C to 95°C, and was kept at 10 : 1 : 1 by weight in order to observe the PVA concentration dependence. For this composition ratio, 1 mol of borate ions is stoichiometrically distributed to 1.89 mol of PVA for A6. Although more than one mole of crosslinking agent per mole of polymer chain is required for gelation as predicted by the classical theory on gels[16,17], the alkaline solutions studied here became gels at moderate temperatures, as shown below. This might be due to the fact that hydrogen bonding plays an important role as well as borate ions in cluster formation of PVA chains, resulting in an increase in apparent degree of polymerization.

Gel–sol transition temperature measurement

The gel–sol transition temperature (T_{gel}) measurement was made by tilting a test tube containing the sample in a temperature-controlled water bath. Although rheological measurements with a cone-plate rheometer were attempted, solidification of PVA made it difficult to obtain quantitative data. T_{gel} obtained by the tilting method was in good agreement with that obtained by a ball-drop method, as reported elsewhere[22].

SANS

The SANS experiment was made at the Research Reactor at the National Institute of Standards and Technology. A flux of cold neutrons monochromatized with a velocity selector of wavelength $\lambda = 9$ Å* was used as an incident beam. Copper sample chambers 2 mm thick and 16 mm in diameter with copper and quartz windows on both sides were designed for this experiment. Two-dimensional scattered intensity data were corrected for background noise, fast neutron scattering, air scattering, transmittance and then averaged circularly so as to obtain one-dimensional data array with respect to the scattering vector. The intensity data were also corrected for solvent and bulk PVA by assuming additivity of the scattered intensity.

SANS experiments were made on both as-prepared (A4 and A6) and aged samples (A4-aged and A6-aged) at many temperatures in order to focus on temperature dependence of the scattering behaviour by elevating temperature step by step. There was no significant difference between the as-prepared and aged samples for alkaline gels. Consequently only the aged samples are discussed here. Thirty minutes were allowed for sample homogenization at a given temperature. Each measurement lasted until the monitor registered 5×10^7 counts, which roughly corresponds to 30 min.

RESULTS AND DISCUSSION

The following facts need to be made clear at this stage before going into the discussion.

(1) PVA-borate gels studied here were prepared by heating PVA aqueous solutions containing borate ions up to the temperature above T_{gel} and then cooled gradually. Therefore the gels studied in this work seem to be homogenized better than gels prepared by chemical reaction.

(2) The sol–gel transition is macroscopically reversible with temperature without significant hysteresis.

(3) The PVA concentrations are above the overlap concentration where individual chains start to overlap.

(4) The classical theory[16,17] indicates that at least one crosslink per chain is required to form an infinite cluster. Since the molar ratio of borate to PVA is 0.529 and 0.705, respectively, for A6 and A4, the borate concentration is not enough to gel the system. Therefore crosslink formation via hydrogen bonding is also expected.

(5) The sol fraction was not excluded from the system so as not to disturb the system. Therefore the PVA-borate systems studied here are considered to be very different from chemical gels prepared by radiation[5] or chemical reaction[8,18] and from simple physical gels like polystyrene in CS_2[25–29].

Gel–sol transition temperature

Figure 1 shows the gel–sol transition temperature curve of the PVA-borate gel. The system was clear throughout the range of observation. The gel–sol transition temperature was macroscopically thermoreversible without hysteresis. It depends on pH, PVA concentration, molecular weight of PVA and boric acid concentration, as was extensively investigated elsewhere[22].

SANS

The scattered intensity is proportional to the structure factor $S(q)$. The contrast factor K is given by

$$K = (N/v_0)[a_{PVA}(v_0/v_{PVA}) - a_{D_2O}]^2 \qquad (13)$$

where N and a_k are the Avogadro number and the scattering length of component k, respectively, v_{PVA} and v_0 are the monomer volume of PVA and the reference

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* 1 Å = 10^{-10} m

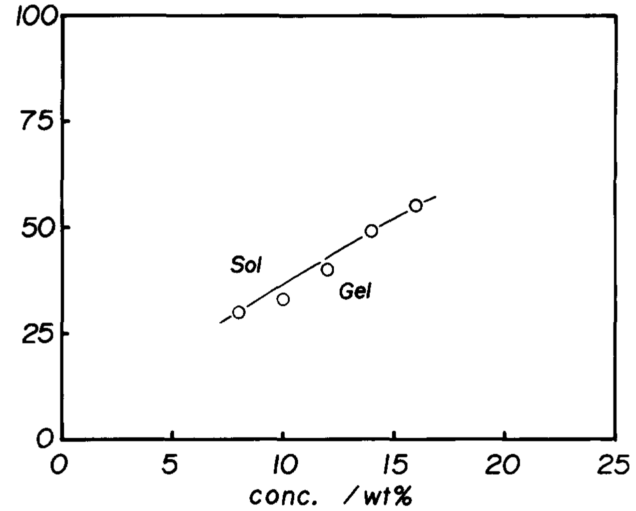

Figure 1 Sol–gel transition curve for PVA-borate gels

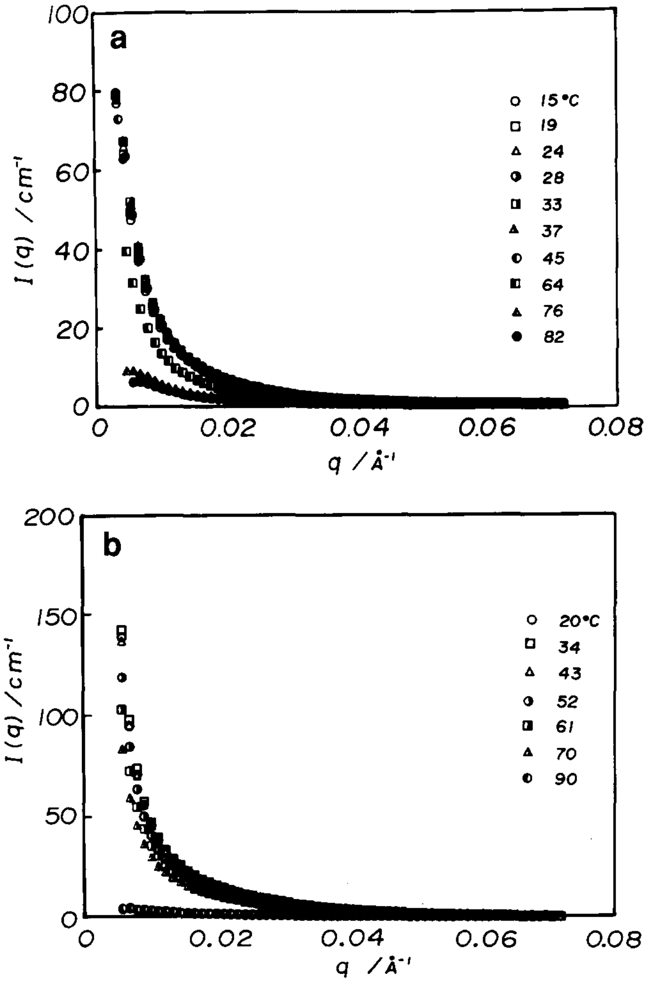

Figure 2 Small-angle neutron scattered intensity curves for (a) A4-aged and (b) A6-aged

(i.e. D_2O) volume, respectively. K is estimated to be $0.0948\,\mathrm{cm}^{-1}$ by assuming that no isotope exchange reaction takes place between the hydroxy group of PVA and D_2O. Therefore this value gives the upper limit of the contrast factor since some amount of isotope exchange reaction is expected in the system. The mass densities of PVA and D_2O are 1.3 and 1.1, respectively. Since the reference volume was chosen to be the monomeric volume of D_2O, c is reduced to the reduced monomer concentration with respect to the volume of a D_2O molecule.

Figure 2a, b shows the scattered intensity profiles of A4-aged and A6-aged at several temperatures. The scattered intensity decreases monotonically with q and shows no scattering peaks. With increasing temperature, the intensity decreases drastically at the low-q-region. For hydrogels, the scattered intensity at given q increased by a factor of more than 50 by ageing for two months at room temperature[30]. This is mainly due to crystallization of PVA. In contrast to this, the alkaline gels were stable over several months by monitoring SANS intensity. Therefore only the alkaline gels were dealt with as model systems of gels.

Since the fractal dimension D is the most important quantity to describe the gel structure, as discussed earlier, it was evaluated first by plotting $\log I(q)$ *versus* $\log q$. *Figure 3a, b* shows double logarithmic plots of the scattered intensity $I(q)$ *versus* the scattering vector q for A4-aged and A6-aged, respectively, at all temperatures studied here. The value of D should be obtained from the slope at the high-q region. However, since the upper limit of the q range was limited in this work, an apparent D was obtained by taking a slope at $q > 0.03\,\text{Å}^{-1}$ ($\log(q/\text{Å}^{-1}) \gtrsim -1.5$). The variation of D thus estimated is shown in *Figure 4*. The sol–gel transition temperature measured by tilting a test tube, T_{gel}, is indicated with an arrow. D seems to be constant and to be around 2.8 ± 0.1 and 2.6 ± 0.1 for A6-aged and A4-aged, respectively,

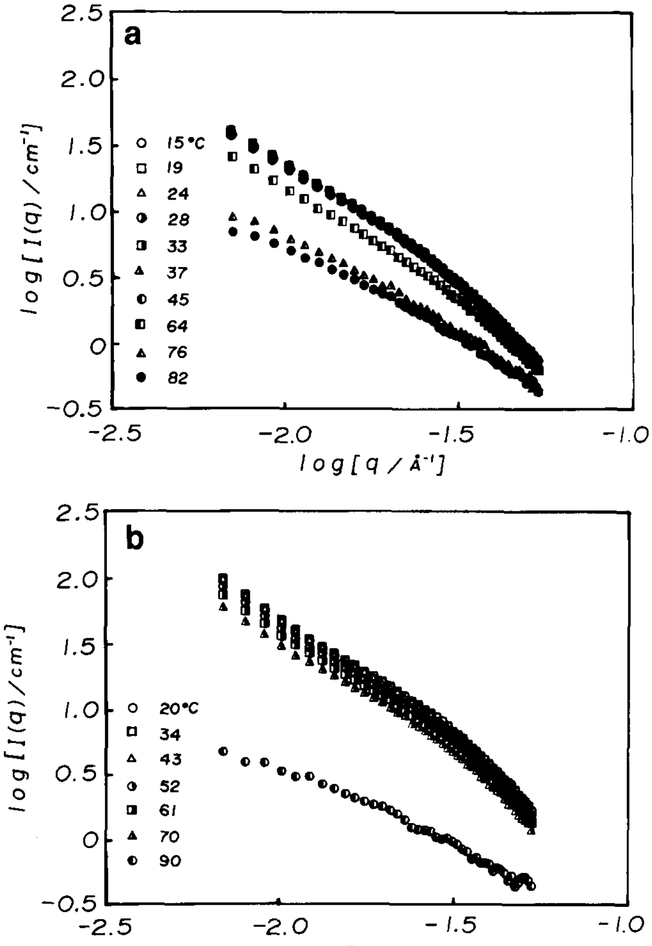

Figure 3 Double logarithmic plots of $I(q)$ *versus* q for (a) A4-aged and (b) A6-aged

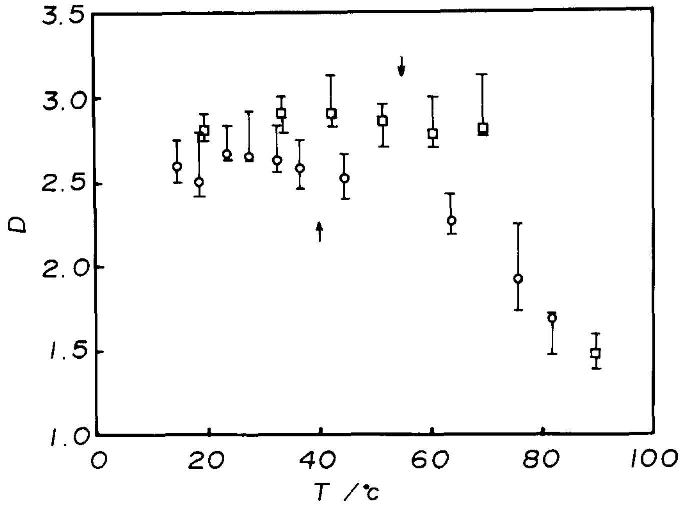

Figure 4 Temperature variation of the apparent fractal dimension D for A4-aged (○) and for A6-aged (□)

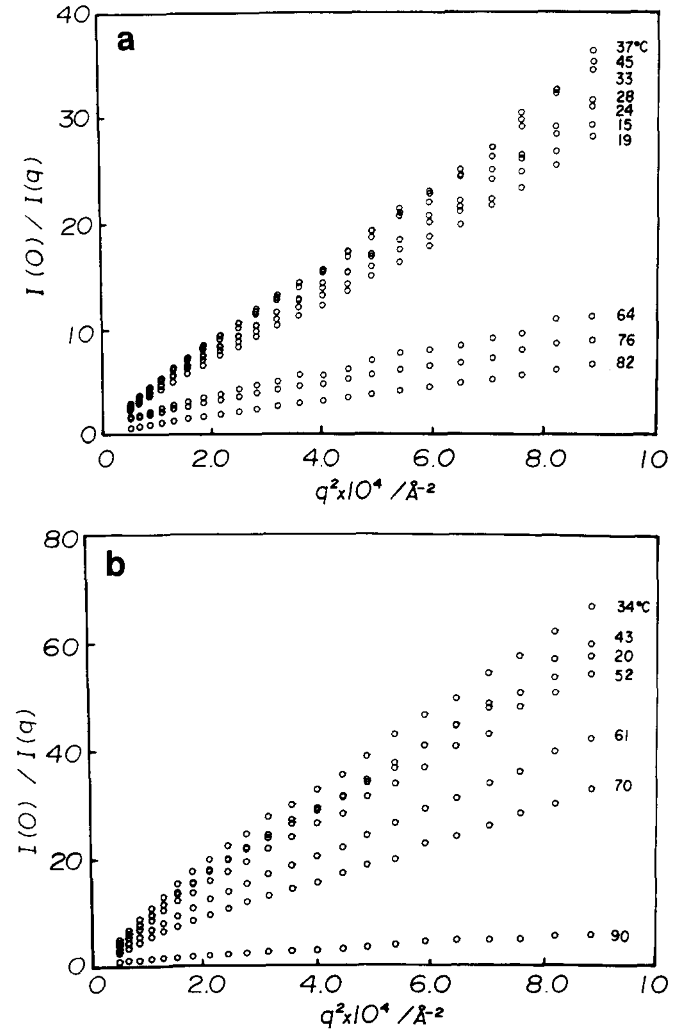

Figure 5 Zimm plots for the scattered intensity $I(q)$ for (a) A4-aged and (b) A6-aged

where $T < T_{gel}$. However, D decreases with T for $T > T_{gel}$. The variation of D in the sol state will be discussed below.

The correlation length ξ can be obtained where structural correlation exists. The apparent correlation length ξ_{app} is obtained from the plot of $I(0)/I(q)$ *versus* q^2 both for gels and sols, where ξ_{app} is estimated from the plot $I^{-1}(q)$ *versus* q^2 as

$$\xi_{app} = |\text{slope}|^{1/2} \qquad (14)$$

Figure 5a,b shows the reduced reciprocal intensity, $I(0)/I(q)$, *versus* q^2 plots for A4-aged and A6-aged, respectively, at several temperatures. Although a slight curvature was seen, the correlation length was estimated by using a low-q region, e.g. 0.006–0.02 Å. For gels, according to equation (3), ξ is given by

$$\xi = [6/D(D+1)]^{1/2}\xi_{app} \qquad (15)$$

The estimated values of ξ for A4-aged and A6-aged gels, however, are more than 100 Å, and are out of the range of the Guinier criterion, i.e. $q\xi < 1$. Therefore, an alternative method was used to estimate ξ. The equation (4) can be written as

$$I(q) = \frac{I(0)}{\left\{1 + \frac{(D+1)}{3}\xi^2 q^2\right\}^{D/2}} \qquad (16)$$

The ratio $I(0)/I(q)$ is thus given by

$$\frac{I(0)}{I(q)} = \left[\frac{D+1}{3}\right]^{D/2} \xi^D q^D \left[1 + \frac{3}{D+1}\frac{1}{\xi^2 q^2}\right]^{D/2}$$

$$\simeq \left[\frac{D+1}{3}\right]^{D/2} \xi^D q^D \qquad \text{for } \xi q \gg 1 \qquad (17)$$

Therefore ξ can be obtained by plotting $\log[I(0)/I(q)]$ *versus* $\log q$.

Figure 6 shows the ξ variation for alkaline gels *versus* temperature. The correlation length seems to be constant both for A4-aged and A6-aged in gel state and decreases with T above the transition temperature (40°C for A4-aged and 55°C for A6-aged). The size of the individual PVA chains is estimated by the z-average radius of gyration for unperturbed PVA chains, $\langle R_g^2\rangle_z^{1/2}$, which was given by

$$\langle R_g^2\rangle_z^{1/2} = b_{PVA}P_z^{1/2}/6^{1/2} \qquad (18)$$

where b_{PVA} is the segment length, estimated from SANS measurement of a 50/50 mixture film of deuterated and hydrogenated PVAs[27]. The estimated radius of gyration is

$$\langle R_g^2\rangle_z^{1/2} = 33.5\ \text{Å} \qquad (19)$$

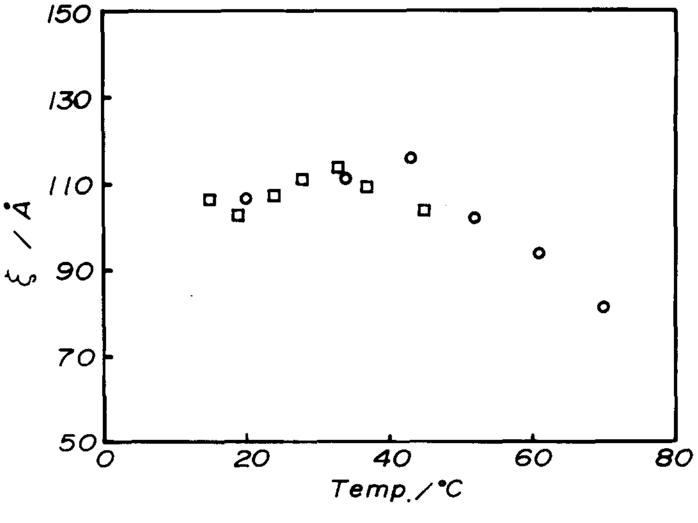

Figure 6 Temperature variation of the correlation length ξ for A4-aged and A6-aged in gel state

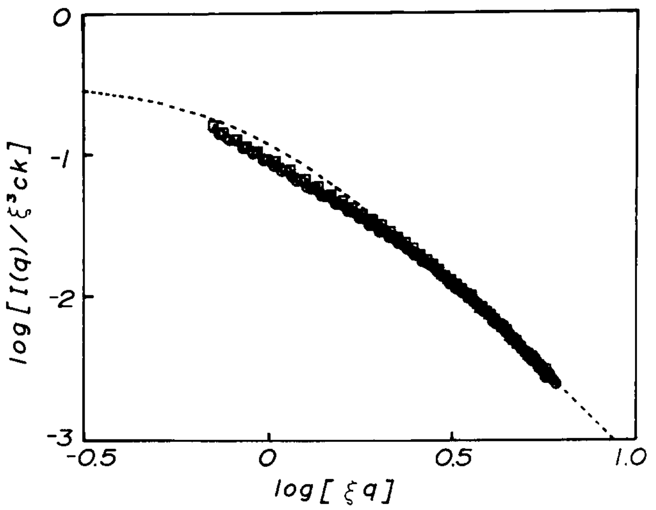

Figure 7 Master curve for A4-aged in the gel state: broken line indicates the theoretical master curve based on equation (4) with $D = 2.6$

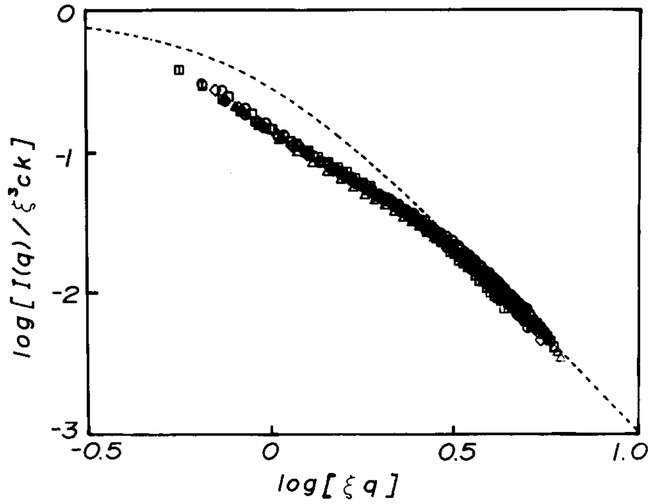

Figure 8 Master curve for A6-aged in the gel state: broken line indicates the theoretical master curve based on equation (4) with $D = 2.8$

In the gel state, the network structure is frozen, hence a constant value of ξ is observed. The infinite clusters are broken into finite clusters around T_{gel}. Although $\xi \approx 19$ Å is expected for molecularly dispersed PVA chains because of the relation $\xi = (1/3)^{1/2}\langle R_g^2\rangle_z^{1/2}$, the observed ξ is still larger than the predicted chain size in sol state. This fact indicates the presence of finite PVA clusters in sol state even at the highest temperature of observation.

Equation (4) predicts that the individual scattered intensity curves for gels can be superimposed to a single master curve by employing the reduced scattering vector ξq, if D is constant irrespective of temperature. *Figure 7* shows plots of $I(q)/\xi^3 ck$ *versus* ξq for A4-aged in double logarithmic scale. The theoretical curve is also drawn with a broken line. As can be seen in the figure, each curve falls onto a single master curve and the master curve is well predicted by the theoretical curve. At high q, the asymptotic behaviour of the master curve has the slope of -2.6 ± 0.1, which recovers the same exponent evaluated on the individual curves for A4-aged. *Figure 8* shows the same plots for A6-aged. Although a systematic deviation from the theoretical curve is detected here, the superposition seems again to be successful. The systematic deviation of the observed data from the theoretical indicates the presence of a different fractal dimension at low q. The fractal dimension observed at high q was 2.8 ± 0.1, as obtained from the corresponding individual curves. The collapse of data for different temperatures in the gel phase in the plot of $I(q)/c\xi^3$ *versus* ξq shows that the gel consists of domains of size ξ and that the domain has an apparent D for distances within the domain. The fractal dimension for chemically crosslinked gel at the gel point is around 2.5 for gels in a reaction bath and 2.0 for the crosslinked clusters in swelling equilibrium[18]. The observed fractal dimension for PVA-borate gels is significantly larger than these values, which may be due to the presence of hydrogen bonding in addition to borate-aided crosslinks, which makes the system more compact. The difference in D between A4-aged and A6-aged indicates that the higher the concentration of PVA, the more compact are the domains.

Martin and Wilcoxon[8] recently reported that the scattered intensity functions for gels could be superimposed by reducing $I(q)$ and q to $I(q)/c\xi^D$ and $q\xi$, respectively. The reducing parameter $c\xi^D$ originates from the relation

$$I(q=0) \sim M \sim \xi^D \tag{20}$$

which has a different background from equation (3). For their study, the superposition seems to be successful. The fractal dimensions, however, obtained from the superposition ($D = 2.3$) is different from the one obtained from the slope of the plot of $\log I(q)$ *versus* $\log q$ plot ($D = 1.8$). They reported that the value $D = 2.3$ was more reliable because of the scatter of the data points at large q.

For the PVA hydrogels, i.e. PVA aqueous gels without borate ions, the variations of ξ and D with temperature are rather complicated because of formation of PVA microcrystallites[24,30,34]. D, for example, was in the order of 3, which is larger than for alkaline gels, and increased by ageing[30,34]. The correlation length and the scattered intensity at $q = 0$, $I(0)$, for a system which had a PVA concentration around the chain overlap concentration showed anomalous temperature dependence. These phenomena were interpreted with a two-phase model of aggregate-rich and -poor phases in the previous paper[24].

Compared with the PVA hydrogels, the PVA alkaline gels studied here seem to be less complicated. PVA-borate gels are composed of space-filled domains (or clusters) having a correlation length of *ca.* 110 Å and each domain is packed more densely than chemically crosslinked gels such as crosslinked poly(tetramethoxysilicon)[3] or polyurethane[6,18].

In the sol state, $S(q)/\xi^x cK$ for each system was plotted as a function of ξq in double logarithmic scale by varying x so as to collapse all the data onto a master curve. The value of x for the best fit should give the exponent τ according to equation (12)

$$x = D(3 - \tau) \tag{21}$$

The best fit was attained when x was equal to 3, as shown in *Figure 9*. D was also estimated from the slope in the high-q region based on equation (12) and was 2.2 ± 0.1 for A4-aged and A6-aged. Thus τ was found to be 1.6 ± 0.1. The value of D in sol state is larger than the value ($D = 2$) for clusters (lattice artefacts)[32,33] below the gel point. This might again result from the presence

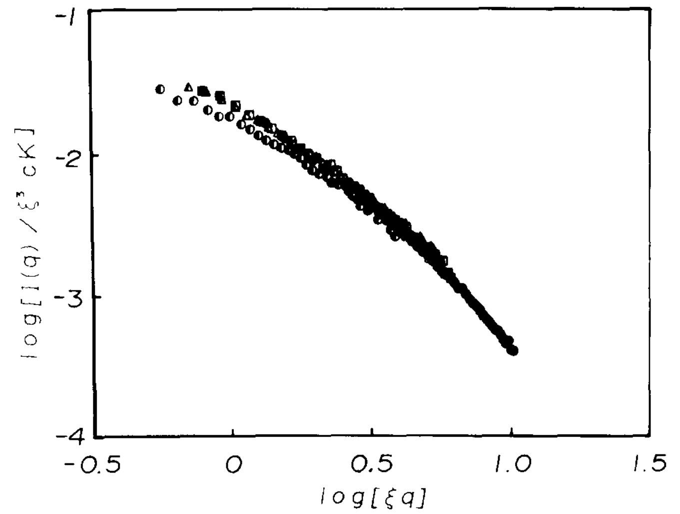

Figure 9 Master curve for A4-aged: (◧) 64°C; (◭) 76°C; (●) 82°C; and A6-aged: (◐) 90°C; in sol state

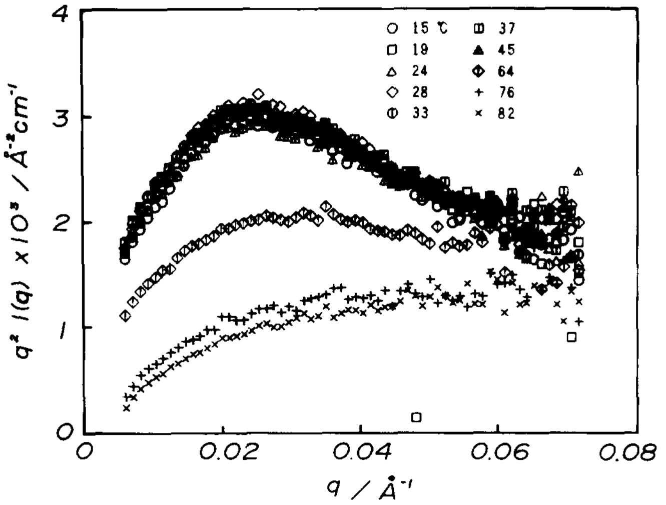

Figure 10 Kratky plots of A4-aged

of hydrogen bonding. All of these facts regarding D show that PVA-borate sol and gel are different from other chemically crosslinked gels such as tetramethoxysilicon gels[8] and polyurethane gels[6,18].

The sol–gel transition from the viewpoint of the classical theories

Here the scattering functions of PVA-borate complex from the viewpoint of the classical theories are discussed. Kajiwara *et al.*[35,36] proposed a scattering function for randomly branched clusters, which is given by

$$I(q) \sim [1 + \alpha\phi(q)]/[1 - (f-1)\alpha\phi(q)] \qquad (22)$$

where f and α are the functionality of the monomer unit and the branching probability, respectively, and $\phi(q)$ is given by

$$\phi(q) = \exp[-q^2b^2/6] \qquad (23)$$

for the chain obeying Gaussian statistics, where b is the segment length of the monomer unit. The equation (22) predicts that the intensity diverges at the gelation threshold, i.e. $\alpha = \alpha_c = 1/(f-1)$. However, it can be extended for gels by defining the criterion as $(f-1)\alpha\phi(q) < 1$. Based on this approach, they fitted the scattered intensity curve for κ-karagenaan aqueous gels with equation (22)[37]. In a Kratky plot ($q^2I(q)$ *versus* q), they found that the scattering curve from a gel had a maximum, whereas that from a sol did not. This could be a useful indication for the sol–gel transition. *Figure 10* shows the Kratky plot of A4-aged. As can be seen, all of the curves except 76 and 82°C show maxima, indicating that those are in gel state. The curve for 64°C seems to be in between the two states. Similar behaviours are also seen for A6-aged. Therefore the Kratky plot could be a useful method to determine the sol–gel transition, although further theoretical developments are required.

CONCLUSIONS

The structure of PVA-borate gels, prepared by cooling PVA-borate aqueous solutions, were investigated by small-angle neutron scattering. The scattered intensity functions for gels at different temperatures could be superimposed by employing reduced variables $I(q)/\xi^3$ and ξq. This indicates that the system is composed of domains of PVA clusters filling the space. The fractal dimensions of PVA inside the domain are 2.6 and 2.8 for A4 and A6, respectively. This suggests that chains in the domain are packed more densely than percolation clusters. In the sol state, the system is described as an ensemble of polydisperse clusters of $D \simeq 2.2$.

All of the facts disclosed in this work indicate that PVA-borate sol and gel are different from most other chemically crosslinked systems such as poly(tetramethoxysilicon) and polyurethane. This might be due to the strong interaction between PVA chains based on hydrogen bonding.

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