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Physical Gels of Aqueous Poly(vinyl alcohol) Solutions: A Small-Angle Neutron-Scattering Study

Wen-li Wu,[*,†] Mitsuhiro Shibayama,[‡] Saroj Roy,[§,⊥] Hidenobu Kurokawa,[‡] Laurence D. Coyne,[†] Shunji Nomura,[‡] and Richard S. Stein[⊥]

Polymers Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, Department of Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto, 606, Japan, and Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: The melting behavior of aqueous poly(vinyl alcohol) gels was studied by using small-angle neutron scattering. Emphasis was placed on solutions with a polymer concentration around ϕ^*, the concentration threshold at which the polymer chains start to overlap. At this particular concentration, a maximum was observed in the polymer–polymer correlation length and the zero angle scattering intensity as the gel was melted. An attempt to interpret this observed maximum in terms of a simple two-phase model will be presented.

Introduction

Physical gelation in various polymer solutions has been a subject of interest to many researchers.[1-4] Poly(vinyl alcohol) (PVA) in water is one of the physical gel systems studied rather extensively;[5-7] after all, PVA fibers have been produced commercially from aqueous PVA solutions for many years. Compared to chemical gelation, the gelation process in physical gels has not been widely studied by scattering techniques. This does not imply that other transitions, e.g., liquid–liquid phase transitions in physical gels, have not been studied with scattering techniques. For instance, the spinodal transition in PVA–water has been determined via an elastic light-scattering technique.[6] For the sol–gel transition problem, the change in the cluster size or molecular weight distribution during gelation is an essential parameter to monitor. The sol–gel transition is defined as the point at which the average cluster size goes to infinity. To measure the molecular weight or the cluster size distribution with either chromatographic or scattering techniques, the material must be diluted. However, dilution will cause physical gels to be highly disturbed or even completely dissolved. Consequently, scattering and other techniques in which dilution is a prerequisite are applicable only in studying the sol–gel transition in chemical gels. However, as will be shown, it is possible to study certain aspects of physics gelation without resorting to a dilution scheme where even the cluster size is inaccessible to the measurements. In other words, it is not the intention of this work to detect the connectivity among the molecules within a cluster using a scattering technique.

The basic process of physical gelation in polymer solutions is the formation of thermally reversible junctions between the molecules. Regardless of the nature or the origin of the junction, the local polymer segment density around a junction point changes from that of a linear chain in solution. For example, in a good solvent the mass fractal dimension, D, is 5/3 and 2 for linear chains and branched ones, respectively.[8] The parameter D is defined as $N \propto r^D$ where N is the number of segments within a volume of r^3 in three-dimensional space considered herein. Accordingly, the local segment density is expected to increase upon interchain cross-linking. For a polymer solution with its concentration near ϕ^* and its temperature above the Θ temperature, the length scale of the density fluctuation is the size of an individual molecular coil. When the temperature is lowered toward its sol–gel transition, some interchain cross-links or junctions are formed among neighboring pairs, and the local segment density is enhanced around the junctions. Solvent-rich regions must be formed surrounding these cross-linked molecules. This is assuming that cross-linking does not perturb the position of any other adjacent molecules not connected directly to the cluster under consideration. According to this picture of cross-linking, the polymer–polymer correlation length must increase, and this change in correlation length should be observable in small-angle scattering (SAS) measurements. In this work, deuterated water was used as the solvent, and neutron scattering was used to determine the temperature dependence of the correlation length. No deuterated PVA was used in this work; therefore, the only correlation mea-

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[*] To whom correspondence should be addressed.

[†] National Institute of Standards and Technology.

[‡] Kyoto Institute of Technology.

[§] Present address: Polaroid Corp., Norwood, MA 02062.

[⊥] University of Massachusetts.

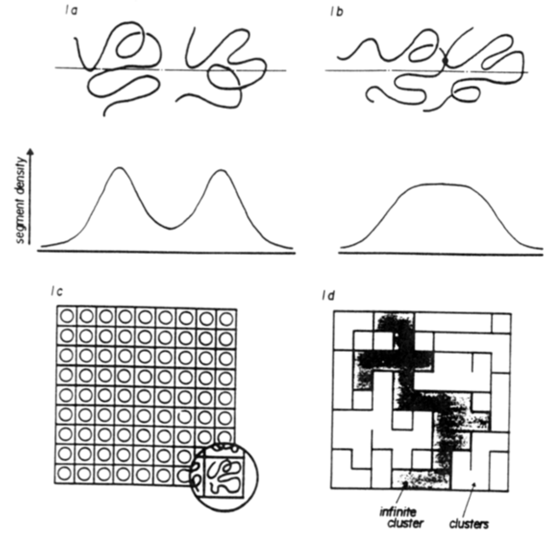

Figure 1. (a) Polymer segment density profile of two neighboring chains in a ϕ^* solution. (b) Same as a except these two chains are now connected by a thermally reversible junction. (c) Ideal lattice model for ϕ^* polymer solutions. Each lattice point is occupied by one chain, and the demarcation lines or the grids denote the solvent-rich region separating polymer chains. (d) Shadowed area represents a polymer cluster bridging both sides of the lattice after the formation of many junctions between lattice points.

sured is the polymer–polymer correlation. Hereafter, the term polymer–polymer will be omitted.

The above statements regarding the change in the correlation length in ϕ^* solutions are not applicable to solutions with concentrations much greater than ϕ^*. In such cases, the number of neighboring chains for any given chain is rather large, and all the chains are highly interpenetrated. Consequently, the formation of physical junctions or cross-links is not likely to induce any significant change in the local segment density distribution or the correlation length. This point becomes obvious as one extrapolates the above argument to the extreme case of high polymer concentration, namely, to the bulk, where cross-linking is unlikely to induce any significant amount of density fluctuation. Cross-linking due to the formation of crystallites is not considered herein; otherwise, it can cause some density fluctuation even in bulk materials.

For those solutions with concentrations well below ϕ^*, the correlation length measured in good solvents is the radius of gyration of an individual chain. Due to geometric constraints, gelation will not occur in solutions with low polymer content, and the molecules will tend to aggregate as the temperature is lowered or the solvent power is decreased. This will result in a monotonic increase in both the correlation length and the apparent molecular weight. These changes can be observed as an enhancement in the zero-angle scattering intensity, even for those polymer–solvent pairs incapable of forming a physical gel. Therefore, one would not expect to gain any new insight into physical gelation from experiments using dilute solutions.

A simplified version of the gelation process in ϕ^* solutions is depicted in Figure 1a–d. The segment density distribution profile for two neighboring chains before the formation of a physical junction is given in Figure 1a. The changes in the segment density profile after the formation of a junction are illustrated in Figure 1b. Note the disappearance of the solvent-rich region between two chains connected by a newly formed junction in Figure 1b. What is not shown in Figure 1b but is essential to this model is the increase of the solvent-rich region due to junction formations. As the junction formation proceeds, more solvent-rich region will be created. Placing molecules in a simple cubic lattice, a polymer solution of ϕ^* concentration in good solvent can be represented as in Figure 1c. Within the present context, the demarcation lines separating each molecule represent the solvent-rich regions or regions depleted in polymer segments. From the arguments represented in Figure 1a and 1b, a gelation process can be considered as the removal of a demarcation line and as a creation and coalescence of solvent-rich regions around the clusters. The gelled state is then represented by Figure 1d. The shadowed area depicts a gel particle bridging the opposite sides of the lattice and hence represents a polymer cluster with infinite molecular weight. The above model resembles a random bond percolation problem; every site is occupied, and the formation of a junction between two neighboring sites is equivalent to the removal of a boundary line. This model will be called the pseudobond percolation, and it is different from the percolation models used in phase transition or other critical phenomena. The formation of a bond involves a change in the shape or the density distribution of the connecting particles for the physical gelation problem whereas no such change is considered in a typical random bond percolation model. Since the SANS measurements were conducted in undiluted systems, the correlation length so obtained is the spatial correlation length, which has no direct relation to the connectivity correlation length or the cluster size.[9]

In the rest of this paper, the experimental results from small-angle neutron scattering (SANS) conducted on samples with polymer concentration around ϕ^* will be reported. A qualitative comparison will be made between the results and the ideas presented in Figure 1a–d.

The temperature for liquid–liquid phase separation, the bimodal temperature, is around 30 °C[6] for aqueous PVA (DP = 500; 15 wt %). The phase separation will surely perturb the gelation process in the aqueous PVA solutions since the sol–gel transition temperature (T_c) of some of the samples studied in this work was found to be above 30 °C. To investigate the possible interaction between the phase separation and the gelation process, two different types of experiments were performed. The first experiments began with PVA in the gelled state, and the dissolution of the gel was monitored. The starting gel was obtained by quenching a 95 °C solution to room temperature; gelation set in quickly after the quenching. The gel stayed clear for a few days at room temperature; this suggested that no massive phase separation or crystallization took place, perhaps due to inhibition from the presence of gels. All the SANS measurements were started within 1 day after the quenching. The information obtained will likely shed some light on the gelation process with minimal interference from the phase separation. The other experiments started with PVA solution at 95 °C. The cooling process was monitored by using SANS. Some of the results will be reported to illustrate the differences between these two types of experiments and the hysteresis effects in gelation and dissolution.

The radius of gyration (R_g) of PVA with a degree of polymerization (DP) = 120 was found to be around 30 Å.[10] Based on this value for R_g and taking the density of PVA to be 1.3, the value of $\phi^* \sim \mathrm{DP}/R_g$ is around 9% by volume for the aqueous PVA solutions used herein. Throughout this work, the polymer concentration is expressed in terms of volume percent. Hereafter, the term volume will be omitted. SANS results from 2%, 6%, 10%,

Table I
Specifications of the Aqueous PVA Solutions Used in SANS Study

sample no.	polymer concn, vol %	sol–gel transition, °C
1	2	below 22
2	6	below 22
3	10	65
4	16	75

and 16% samples will be presented. It is believed that these concentrations will encompass the value of ϕ^* even though the definition of ϕ^* is approximate. It is not the purpose of this work to identify the "true" value of ϕ^* with one of the concentrations used in the SANS measurements.

Experimental Section

Material. Commercially available PVA powders with a degree of polymerization (DP) of 120 were supplied by Unitika Chemical Co., Ltd.,[17] Japan. The degree of saponification is 99.87 mol %, and the triad tacticity is 21.6% (iso), 48.9% (hetero), and 29.8% (syndio),[11] values typical for poly(vinyl alcohol) prepared from saponification of poly(vinyl acetate). The polydispersity of this polymer is about 2.0 as measured by GPC.

Sample Preparation. To avoid inhomogeneity and local gelation, deuterated water solutions of PVA were prepared at 95 °C under constant stirring for 3 h. Deuterated water containing more than 99% deuterium was purchased from Cambridge Isotope Laboratories, Inc.[17] The concentrations of the samples used in the neutron-scattering experiments are listed in Table I. The sol–gel transition temperature depends upon the PVA concentration and the degree of polymerization as reported elsewhere.[7,11] The sol–gel transition temperature (T_c) measurement was carried out by tilting a test tube containing the sample in a temperature-controlled water bath. One day after quenching from 95 °C to room temperature, the gel was gradually heated in a water bath. The T_c data are given in Table I. Those samples with a concentration of 6% or less tended to separate into two phases at room temperature; they did not form homogeneous or one-phase gel. Under the premise that gelation will not occur in solutions with concentration below ϕ^*, one expects the value for ϕ^* to be above 6% for the polymer used in this work. Hereafter, the term hydrogel will be used for those quenched samples with concentrations greater than or equal to 10%.

Small-Angle Neutron-Scattering Measurement. The neutron-scattering experiment was carried out at the small-angle neutron-scattering facility at the National Institute of Standards and Technology (formerly the National Bureau of Standards). The previously prepared solutions were reheated to 95 °C for 1 h under constant stirring and transferred to quartz cells of 2-mm beam path and quenched in a water bath at room temperature 24 h prior to the SANS measurements. Two-dimensional scattered intensity data were corrected for empty cell scattering, incoherent scattering, and transmittance. All the scattering intensity data were reduced to an absolute scale by using a silica gel as the secondary standard which had been calibrated against a vanadium single crystal.

The time required for the SANS measurements at each temperature varied from 0.5 to 2 h depending upon the polymer concentration and the measurement temperature. Each SANS measurement was started 30 min after the set temperature was reached in order for the structure of the PVA gel to reach thermal equilibrium. Within each measurement, the total scattering intensity was summed every 6 min. For all the runs, a variation in the total count of no more than a few percent was observed. This suggested that during an individual SANS measurement the change in the gel structure was insignificant.

Results

Correlation Length. Figure 2 shows the scattered intensities of the sample with 10% polymer concentration at temperatures from 22 to 95 °C. The scattered intensity decreases monotonically with q for all temperatures. The quantity q denotes the magnitude of the scattering vector and is defined as $(4\pi/\lambda)\sin\theta$, where λ is the neutron wavelength and θ is the scattering angle. With increasing temperature, the intensity curves stay almost unchanged until 80 °C, after which a drastic decrease of the intensities occurs in the low-q region. Similar behavior was observed in all PVA gels studied so far.

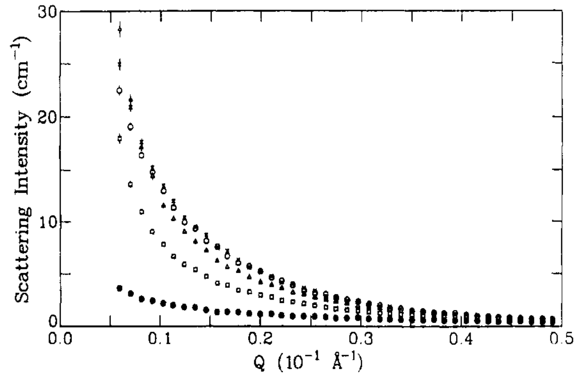

Figure 2. Small-angle neutron scattering (SANS) results of the 10% aqueous PVA solution in a heating cycle. The scattering intensity is expressed in absolute units: (○) 22 °C; (×) 42 °C; (△) 70 °C; (□) 83 °C; (●) 95 °C.

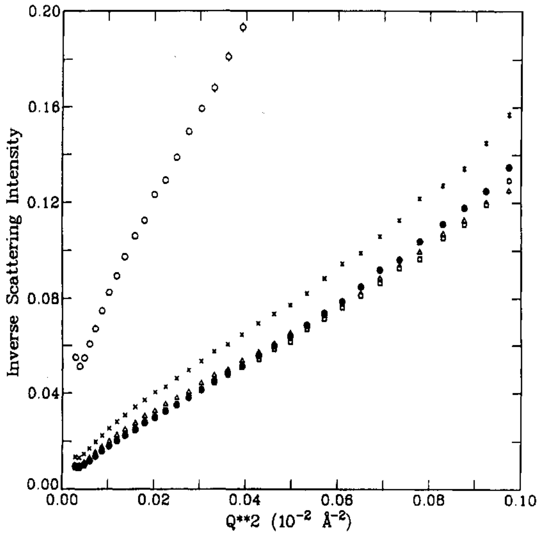

Figure 3. SANS results of the 16% aqueous PVA solution in a heating cycle. These results are plotted as $1/I(q)$ versus q^2: (●) 30 °C; (□) 50 °C; (△) 70 °C; (×) 85 °C; (○) 95 °C.

Figure 3 shows a set of Zimm plots for the sample with 16% polymer concentration measured at five different temperatures from 30 to 95 °C. This figure clearly shows that over the low-q region the correlation length ξ' can be estimated by using the following equation:

$$\frac{1}{I(q)} = \frac{1}{I(0)}(1 + \xi'^2 q^2) \qquad (1)$$

$I(0)$ is the zero q or zero-angle intercept of the scattering intensity. The correlation length, ξ', is a measure of the heterogeneity of the system; it has a simple definition only for dilute solutions. In such cases, the correlation length ξ' equals the average size of an individual molecule or cluster. For semidilute solutions or gels, the physical meaning of ξ' merits further discussion, and this will be addressed in the Discussion section. Figure 4a shows the temperature dependence of ξ' for the quenched aqueous PVA solutions at four different concentrations. The most striking feature is the appearance of a maximum in ξ' for the hydrogel containing 10% polymer. For

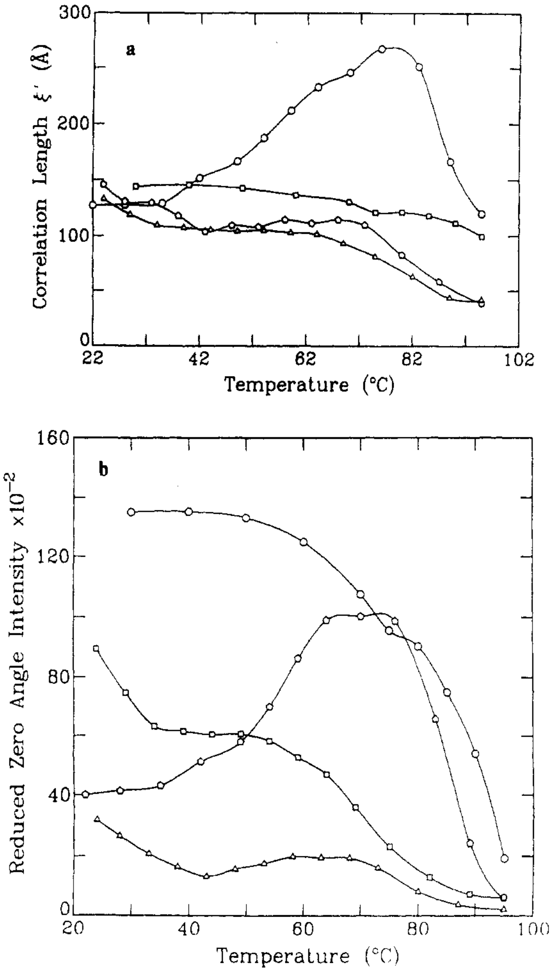

Figure 4. (a) Temperature dependence of the SANS correlation length, ξ', measured from aqueous PVA solutions at four different polymer concentrations. Data collected in a heating cycle: (□) 16%; (○) 10%; (△) 6%; (⬠) 2%. (b) Temperature dependence of the SANS molecular weight calculated from the zero-angle intercepts $I(0)$ of aqueous PVA solutions at four different polymer concentrations. Data collected in a heating cycle: (○) 16%; (⬠) 10%; (△) 6%; (□) 2%.

all other concentrations either above or below 10%, the temperature dependence of ξ' is rather smooth. At the highest test temperature of 95 °C, the value of ξ' is about 100 Å for both the 10% and 16% samples. On the other hand, the value of ξ' for the 2% and 6% samples approaches 30 Å, the value of R_g at high temperature. This agreement between R_g and the correlation length is expected for dilute solutions with good solvents as mentioned earlier.

The q range used to determine ξ' was from 0.005 to 0.012 Å^{-1}. For those samples with ξ' greater than 100 Å, this q range is too high for a precise measurement. Other measurements, especially light scattering, will be more desirable in this respect.

Reduced Degree of Polymerization. Values of the zero-angle scattering intensity $I(0)$ were also obtained as a byproduct of calculating ξ' with eq 1. Since all the scattering intensities have been reduced to the absolute scale, we can obtain quantitative information of the polymer molecular weight from the values of $I(0)$. If the molar volume of deuterated water is chosen as the reference volume and 1.3 as the density of PVA, the average molecular weight of PVA is expressed in terms of this reference volume. This results in a value of 223 for the PVA chains. This quantity indicates that the molar volume of an average chain is 223 times the reference volume, and it will be referred to as the reduced degree of polymerization.

Assuming no interchange between the deuterium of the deuterated water and the hydrogen of the hydroxyl group on the PVA chains, the scattering contrast factor per reference volume is denoted as ΔB^2 and equals 0.069 cm^{-1}. The zero-angle intensities, $I(0)$, after being normalized by the concentration factor $\phi(1 - \phi)$ and by the contrast factor ΔB^2 are given in Figure 4b. In dilute solutions with good solvent, the value of $I(0)$ so reduced is expected to be 223 for the current system. For concentrated solutions with good solvent, this reduced $I(0)$ should be smaller than that of an individual chain. The fact that the values of reduced $I(0)$ given in Figure 4b are all greater than 223 indicates that the polymer chains are aggregated. Since deuterium-hydrogen interchange is inevitable, this estimated contrast factor must be the upper limit. Accordingly, these reduced values of $I(0)$ calculated on the basis of this contrast factor stand for the lower limit of its real value.

The temperature dependence of reduced $I(0)$ shown in Figure 4b is rather similar to the behavior of ξ'; a maximum exists for the 10% sample. For the 6% sample, there is a hint of a weak maximum. For all other samples, the general trend is a smooth decrease in $I(0)$ as the temperature is increased. At 95 °C, the values of $I(0)$ tend to converge toward the molecular weight of an individual chain of 223. For the 2% and 6% samples, another transition is seen in Figure 4b; around 30 °C the values of $I(0)$ show a pronounced decrease with rising temperature. This temperature is rather close to the Θ temperature of PVA in water and is also close to the liquid–liquid phase separation temperature as well.

SANS measurements were also carried out on some samples during the cooling cycle from 95 to 30 °C. The average cooling rate was rather low; typically cooling took 5–10 h including the SANS measuring time at multiple intermediate temperatures. The values for the correlation length ξ' and the reduced $I(0)$ for the 10% sample measured during a cooling cycle are presented in parts a and b of Figure 5, respectively, along with the results obtained from the heating cycle of the quenched gels. These results show a gradual increase in both $I(0)$ and ξ' during the later stage of the cooling cycle. This observation suggests the development of heterogeneities, and this issue will be addressed later.

Discussion

The result shown in Figure 2 was obtained from a 16% hydrogel. The scattering intensity in the $q < 0.03$ Å^{-1} region is highly temperature dependent, and the intensity stays almost unchanged above this q value. This phenomenon was a common one for all the concentrations studied. It strongly suggests that the origin of this temperature dependence of the intensity involves a size scale of 30 Å or above, which coincides with the R_g of the individual chain. No small-scale or local chain aggregation such as microcrystallite or fringed micelle formation was substantiated by this observation. Therefore, the only model considered in this work is a weak junction model as proposed in Figure 1.

With the exception of the 10% sample, the SANS results for the heating of the quenched PVA solutions and hydrogels (Figure 4a,b) can be understood easily. Both the correlation length ξ' and $I(0)$ moved toward those of the single chain due to the improvement in the solvent power as the temperature was increased. At the highest experimental temperature of 95 °C, the values of both ξ' and $I(0)$ are still higher than those for the single chain in all

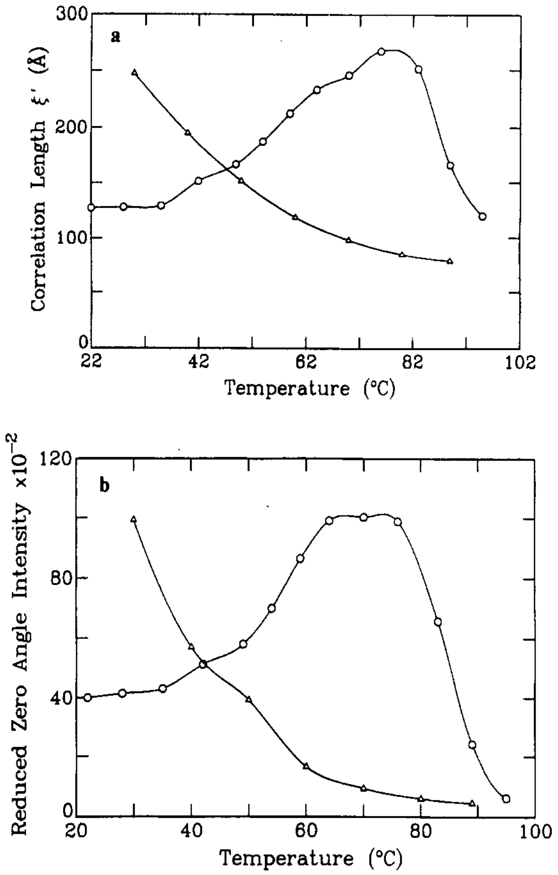

Figure 5. (a) Temperature dependence of the SANS correlation length ξ' measured in the 10% aqueous PVA solution in both a heating (○) and a cooling (△) cycle. (b) Temperature dependence of the SANS molecular weight measured from a 10% aqueous PVA solution in both a heating (○) and a cooling (△) cycle.

of the samples. This unequivocally demonstrates that the PVA chains are still clustered, which may be due to the presence of hydrogen bonding, even at this high temperature.

The anomaly of the 10% sample is rather interesting; a maximum is present in both ξ' and $I(0)$ as the temperature rises. One could explain this anomaly in the following way. The starting gel was obtained by quenching from a 95 °C solution; this gel was expected to be more homogeneous than that from a slow cooling as shown by the data of Figure 5a. The correlation length at room temperature was lower for the quenched gel than that of the slowly cooled one. As the temperature of the quenched gel was raised, one would expect to observe some development of heterogeneities as existed in the slowly cooled one. This accounts for the increase of $I(0)$ and ξ' in the initial part of the heating process. As to the final decrease of $I(0)$ and ξ' as the temperature approached 95 °C, this could be explained by the argument that as the temperature rose some of the gel structure would dissolve and the scattering intensity would approach that of polymers in good solvents. The above explanation sounds reasonable but fails to explain the fact that the maximum was absent in the samples with concentrations above or below 10%.

From a thermodynamic point of view, if one ignores gelation completely, the temperature dependence of $I(0)$ and ξ' is rather straightforward. A monotonical decrease in both $I(0)$ and ξ' with increasing temperature is expected regardless of the polymer concentration. That is not what we observed in this study. In the following, we will extract some additional information from the SANS results collected during the heating of the 10% sample. For this purpose, a two-phase model will be introduced to facilitate the analysis of the SANS data. The purpose of this exercise is to obtain a clearly geometric description of the gel melting process based on the observed temperature dependence of $I(0)$ and ξ'. Such a description is needed before one attempts to comprehend the kinetic or the thermodynamic aspects of this rather intricate gel system.

The model chosen to describe a polymer gel or a partially segregated solution is a two-phase model: one is a polymer-rich phase and the other is a polymer-depleted phase. Within a polymer-depleted domain, the center of mass (CM) values of polymer chains are by definition excluded, whereas in a polymer-rich phase the CMs of chains are assumed to distribute randomly. The advantage of considering the CM of each chain instead of each individual segment in this two-phase model is that the model allows for a smooth transition in terms of polymer segment density at the interface between these two phases. Consequently, the scattering intensity in the high-q region will not follow a q^{-4} law. This is true regardless of the choice of the correlation function for this "two-phase" system.

Let the volume fraction of the polymer-rich phase be C and the correlation function for describing the geometric factor of this two-phase system be $\gamma(r)$. The correlation length of function $\gamma(r)$ is ξ. The rest of the work is to relate C and ξ of the model to the observed $I(0)$ and ξ'. The scattering intensity of such a gelled or segregated polymer solution can be expressed as[15]

$$\frac{I(q)}{\Delta b^2} = \phi N_w P(q) + \phi^2 P(q) \int [1 - \gamma_0(r)] Z(r) e^{-iqr}\, dr \qquad (2)$$

where N_w denotes the weight-average degree of polymerization and $P(q)$ is the normalized single-chain form factor which is assumed to stay unchanged during gelation. $\gamma_0(r)$ accounts for the correlation hole effect between individual chains, as described elsewhere.[14] Its correlation length is the radius of gyration of an average chain. $Z(r)$ stands for the conditional probability function for the following event: given that a starting point is inside the polymer-rich phase, the point at a distance r away is also within the polymer-rich phase. This probability function $Z(r)$ can be related to the correlation function $\gamma(r)$ as follows:[15]

$$Z(r) = 1 + \frac{1 - C}{C}\gamma(r) \qquad (3)$$

For a homogeneous polymer solution, the value of C is unity, and this will convert eq 2 back to a typical Zernike–Prins form.[15] The correlation function $\gamma(r)$ is assumed to be of a Debye type, i.e., equal to $\exp(-r/\xi)$. The choice of this function form for $\gamma(r)$ is not a critical one since only the values of the zero-angle intensity and the initial slope will be addressed in this work. Consequently, the chord lengths or the average dimensions for the polymer-rich and -depleted phases are $\xi/(1 - C)$ and ξ/C, respectively. The chord length[15] is defined as the average dimension of an object between two interfaces. The rest of the work is to derive the relation among C, ξ of the two-phase model, and $I(0)$ and ξ' from the SANS results.

Substituting eq 3 into eq 2 yields

$$\frac{I(q)}{\Delta b^2} = \phi N_w P(q) - \phi^2 P(q) f\gamma_0(r) + \frac{1 - C}{C}\phi^2 P(q) f([1 - \gamma_0(r)]\gamma(r)) \qquad (4)$$

where f denotes the Fourier transform. The first two terms of eq 4 account for the scattered intensity of an ideal solution. Hereafter, they will be replaced by $\phi(1-\phi)N_wP(q)$. The last term accounts for the enhancement in scattering intensity due to segregation or gelation. Under the assumption that ξ is much greater than R_g, the last term can be approximated as $\phi^2[(1-C)/C]P(q)[8\pi\xi^3/(1+\xi^2q^2)^2]$. This will result in a final expression for a phase-segregated solution of

$$\frac{I(q)}{\Delta b^2} = \phi(1-\phi)N_wP(q) + \frac{\phi^2(1-C)}{C}P(q)\frac{8\pi\xi^3}{(1+\xi^2q^2)^2} \qquad (5)$$

The molar volume, v_{D_2O}, of deuterated water is chosen as the reference volume. The term Δb^2 is usually multiplied by v_{D_2O} in the treatment of polymer scattering problems. This product is denoted as ΔB^2, and eq 5 can be rewritten as

$$\frac{I(q)}{\Delta B^2} = \phi(1-\phi)\left(\frac{N_w}{v_{D_2O}}\right)P(q) + \frac{\phi^2(1-C)}{C}P(q)\frac{8\pi\xi^3}{(1+\xi^2q^2)^2v_{D_2O}} \qquad (5')$$

According to the gelation model of Figure 1, the values of N_w and $P(q)$ of the above equation are equal to those of the individual molecule before gelation. This assumption is based on the fact that the polymer concentration is in the vicinity of ϕ^* and the value for C, the volume fraction occupied by the polymer-rich region, is close to unity, as to be proved later.

Equation 5′ was further simplified to a Zimm type expression by replacing $P(q)$ with $1 - q^2R_g^2/3$:

$$\frac{\Delta B^2}{I(q)} = E + Fq^2 \qquad (6a)$$

where

$$E = \frac{(1-\phi)\phi N_w}{1-\phi+\phi N_w} + \frac{1-C}{C}\phi^2\frac{8\pi\xi^3}{v_{D_2O}} \qquad (6b)$$

$$F = \frac{R_g^2(1-\phi)^2\phi N_w}{3(1-\phi+\phi N_w)^2} + \frac{1-C}{C}\phi^2\frac{8\pi\xi^3}{v_{D_2O}}\left(\frac{R_g^2}{3} + 2\xi^2\right) \qquad (6c)$$

At every measurement temperature, there are two experimentally measured quantities related to E and F by fitting the SANS data to a Zimm type expression (eq 1): the quantity $I(0)$ equals $1/E$ and ξ' equals $(F/E)^{1/2}$. There are also two unknowns, C and ξ, in eq 6b and 6c. The best fit results for C and ξ are given in Figure 6a,b. The value of C increases monotonically from its room temperature value of 0.94 toward unity at 95 °C, whereas ξ still exhibits a maximum in the 70–80 °C range.

The result of the temperature dependence of C is of particular interest since it demonstrates that the heating of this hydrogel from room temperature is simply a dissolution process in spite of the peculiar temperature dependence exhibited by the correlation length ξ' and $I(0)$. On the basis of the theoretical relations among ξ, C, ξ', and $I(0)$ (eq 6b and 6c), the maximum observed in ξ' and $I(0)$ can be attributed to the behavior of ξ shown in Figure 6b. The remaining question is the origin of the maximum exhibited in the temperature dependence of ξ introduced in this two-phase model. The pseudobond percolation model mentioned in the Introduction will be reexamined for a possible clue.

Since the value of C is close to unity at all temperatures, the value of ξ is therefore close to the chord length, l_s, of the solvent-rich or polymer-depleted phase. As mentioned earlier, these two quantities are related through a simple relation, $\xi = Cl_s$. The physical meaning of l_s merits further consideration; if the solvent-rich domain is a group of interconnected channels or some ramified branches, by definition l_s is close to the width of an individual channel instead of the size of the whole object. This difference between l_s and the radius of gyration of a ramified or branched object is essential for this work; the average size or the connectivity correlation length of the cluster approaches infinity near the critical point, while the chord length of the cluster increases continuously beyond the critical point. This problem of the chord length in this pseudobond percolation model will be addressed quantitatively next to illustrate the point just mentioned.

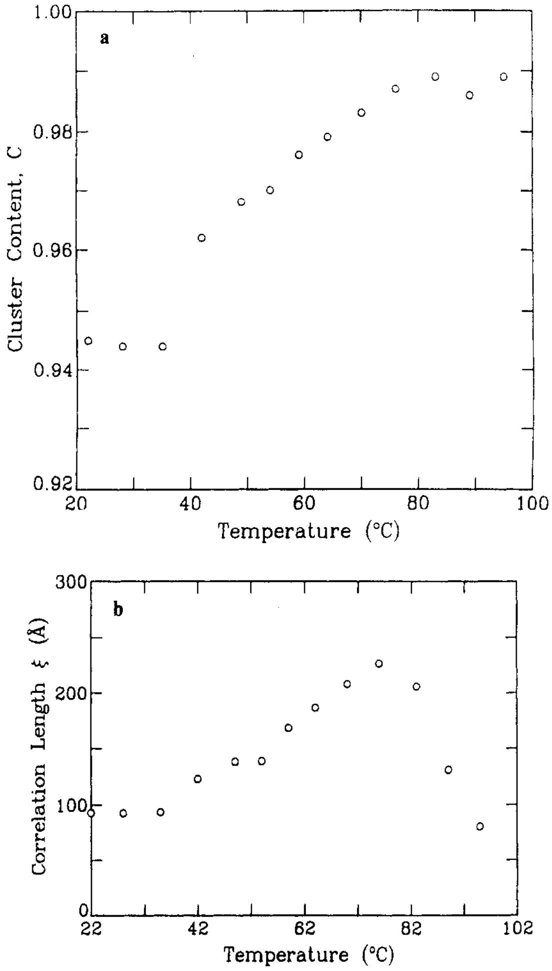

Figure 6. (a) Temperature dependence of the volume fraction, C, occupied by the polymer-rich phase. These calculated results are based on a two-phase model and on the SANS data from the 10% aqueous PVA solution in a heating cycle. (b) Temperature dependence of the correlation length, ξ, introduced in the two-phase model. The calculation was based on the SANS results from a 10% PVA solution in a heating cycle.

The starting material is a group of chains with linear dimension R_g which occupies a volume fraction C. In the midst of a random bond formation, the probability of the existence of any bond between two adjacent particles is P. The probability of finding S connected particles along any direction is $(1-P)^2P^s$. The term $(1-P)^2$ denotes the fact that at both ends of the string of length S the bonds are open. With a simple algebraic manipulation, the average value of S, or the chord length, is found to be $A/(1-P)$ and the correlation length ξ is simply $(1-C)R_g/(1-P)$. In a classical simple site percolation model, C equals P. Consequently ξ will stay unchanged throughout the whole process. In the present case, the volume fraction occupied by a solvent-rich region, $1 - C$, decreases as temperature increases, while the fraction of open bonds, $1 - P$, increases. The observed relation between C and temperature is given in Figure 6a. On the basis of the current model and the relations among ξ, C, and P, we expect that the correlation length measured by scattering experiments in an undiluted reaction bath increases monotonically and diverges only at the very end of the reaction (i.e., $P = 1.0$), instead of at some intermediate value of P, namely, the gelation or the percolation threshold P_c. Hence, the presence of a maximum in the temperature dependence of $I(0)$, ξ', and ξ in the 10% hydrogel is not an inherent property of the pseudobond percolation model.

On the other hand, the value of the correlation length measured in a slow cooling cycle (Figure 5a) tends to support the prediction that $\xi \propto R_g/(1 - P)$. In polymer solutions slowly cooled from a high temperature, the polymer molecules may have enough mobility to attain the equilibrium condition ascribed by the pseudobond percolation process.

According to the calculated result of C (Figure 6a), the heating of the hydrogel at $\phi = \phi^*$ is a simple dissolution process. The remaining question is what kind of dissolution leads to an increase in the correlation length ξ in the early stage. One possibility is that the initial melting of the gel involves the change of a ramified structure to a compact one. In other words, the thin branches of the solvent-rich domains or cluster start to disappear and leave behind a more solid object as commonly observed in the melting of semicrystalline polymers. More work is needed to address this explanation.

Summary

For the sample with its concentration around ϕ^*, a maximum in both $I(0)$ and ξ' was observed during the melting of the hydrogel. Based on a two-phase model, the correlation length ξ and the volume fraction occupied by polymers were calculated. The results of this two-phase model calculation indicate that the heating of this hydrogel results in a gradual dissolution of the gelled phase despite the peculiar behavior exhibited in $I(0)$ and ξ'. The presence of the maximum in $I(0)$ and ξ' is not a direct consequence of the pseudobond percolation model proposed in this work. Instead, a specific dissolution process is needed to explain this observation.

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(17) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply necessarily that the materials or equipment identified are the best available for the purpose.

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