Phase Transition of Submicron Gel Beads

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ABSTRACT: A phase transition of spheres of ionized *N*-isopropylacrylamide gels with diameters ranging from 0.2 to 1 μm has been observed with photon correlation spectroscopy. The submicron gels undergo a sharp, but continuous volume phase transition in water in response to temperature change. The transition temperature depends on the degree of ionization of the gel and is approximately 34 °C for a nonionic gel and 38 °C for a gel with 4.5% ionizable groups. The volume change at transition increases with ionization of the gel. Larger size gels made by the same emulsion polymerization method are studied under the microscope for comparison. The light scattering and microscopic data show excellent agreement.

Introduction

Recently, the volume phase transition of polymer gels has been the subject of great interest because of its scientific and technological importance.[1] The volume of a gel changes discontinuously up to 1000 times when temperature, solvent composition, pH, or ionic composition are changed monotonically near the transition threshold.[1-8] The volume change at the transition increases with the amount of ionized groups incorporated within the polymer network.[2] The phenomenon has been shown to be universal to all gels, as evidenced by various synthetic gels and ones made of natural polymers[9] and has theoretically been identified as a phase transition similar to the gas–liquid phase transition.[2]

The finding of a large volume change in response to an infinitesimal alteration in environment has opened the door to a wide variety of possible applications of gels as functional elements. For example, gels may be used as sensors, switches, or mechanochemical actuators. For such technological applications of the phenomenon, it is naturally desirable that its response time be as short as possible. The kinetics of the discontinuous volume phase transition of gels has not yet been fully understood, but the physical principles underlying the kinetics of continuous volume transition have been clarified.[10,11] The motion of the polymer network of a gel during the time course of swelling and shrinking, is described by a diffusion equation, called a collective diffusion equation, where the diffusion coefficient is defined as the ratio of the osmotic bulk modulus K of the polymer network and the frictional coefficient between the polymer network and liquid.[10] The frictional coefficient f is defined as the ratio of a force F exerted on the liquid while the network is held fixed and the relative velocity v of the liquid and network for a unit volume of the network: $f = F/v$. Because it is a diffusion process, the time needed for a gel to change its volume and shape is proportional to the square of a characteristic length of the gel.[10]

$$\text{time} = (\text{length})^2/(K/f) = (\text{length})^2/D_c \qquad (1)$$

For a spherical gel, the time is proportional to the square of its radius. The diffusion coefficient has been shown to strongly depend on the state of the gel.[11] In particular, it diminishes at the critical point, at which the swelling and shrinking become infinitely slow.

In the case of the discontinuous volume phase transition, the situation is much more complicated due to the formation and evolution of a surface pattern that is a result of mechanical instability associated with large osmotic pressure gradients within the gel.[12] Moreover, since the volume change is extremely large, the diffusion coefficient can no longer be considered to be constant. However, roughly speaking, the square-length law seems to hold if the initial and final states of a transition are fixed.[13] The diffusion coefficient, D_c, of a gel is usually on the order of 10^{-7} cm^2/s. From eq 1 the time needed for volume change is 10^7 s for a spherical gel of 1-cm radius but is only 10^{-3} s for that with 1-μm radius.[10] Because submicron gels have such a fast response, the preparation and determination of their physical properties are of substantial technological importance.

In this paper, we present the preparation and study of equilibrium properties of submicron gel beads of radius ranging from 0.2 to 1μm using photon correlation spectroscopy (PCS). Copolymer gels of *N*-isopropylacrylamide (IPA) and ionizable sodium acrylate gels were used, since they, in macroscopic size, are known to undergo discontinuous volume phase transition in pure water in response to temperature changes.[3] We chose the preparation method carefully. When IPA gels are made at high temperature, the gels formed are opaque. This is due to the fact that at higher temperatures IPA polymer is not soluble in water and hence a phase separation occurs. To obtain homogeneous IPA gels the preparation temperature should be well below the LCST (lower critical solution temperature). When the polymer is water soluble, the usual way to make submicron gel beads is to use the inverse emulsion polymerization technique. We chose nonionic surfactants because ionic surfactants may not allow a stable emulsion state with the electrostatic interaction between ionic groups in a micelle of pregel and ionic surfactants.

Sample Preparation

We prepared submicron gel beads by inverse emulsion polymerization at room temperature. Hexane was used as a solvent. We tried various nonionic surfactants as emulsifiers and found SPAN 20 (sorbitan monolaurate) to be best suited for our purpose. *N,N'*-methylenebis(acrylamide) (BIS) was used as a cross-linker. To incorporate ionic groups in gels, *N*-(acryloxy)succinimide (AOSI) was copolymerized with IPA.[14] AOSI is known to be easily hydrolyzed under slightly basic conditions.[14] Ammonium persulfate (AP) was used as an initiator. The concentrations of monomers in pregel solutions were chosen to be the same as those for bulk gels studied previously,[3,4] that is, 700 mM for IPA, 8.6 mM for BIS, and 0, 8, 16, and 32 mM for AOSI. *N,N,N',N'*-Tetramethylethylenediamine (100 μL) was added to the mixture of the hexane–SPAN 20–pregel system (hexane, 40 mL; SPAN 20, 0.25 g; pregel, 3.0 mL) to accelerate the polymerization. The solution was stirred by a magnetic stirrer for 4 h. After the gel beads were washed and dialyzed in pure water, they were hydrolyzed in 10^{-2} M NaOH aqueous solution, converting the side group into COO$^-$Na$^+$.

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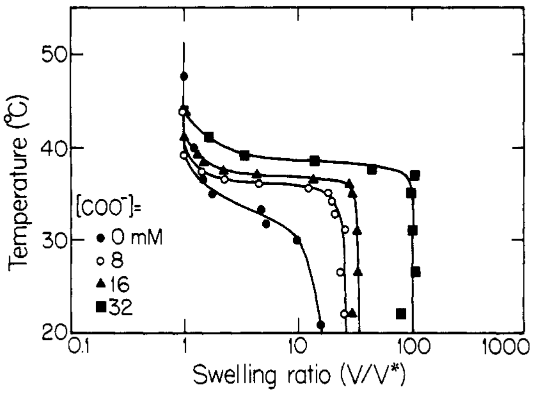

Figure 1. Equilibrium swelling ratio V/V^* of ionized *N*-isopropylacrylamide submicron gels made by inverse emulsion polymerization plotted against temperature. Ionic groups are introduced by copolymerization with *N*-(acryloxy)succinimide, the side group of which is later converted to $COO^-\ Na^+$ by hydrolysis. Swelling ratios V/V^* are calculated from the hydrodynamic radius as determined by photon correlation spectroscopy, where V^* is the collapsed volume. Lines are guides for the eye.

Photon Correlation Spectroscopy

The hydrodynamic radius of the submicron gel beads was measured by means of photon correlation spectroscopy (PCS). Solutions containing the sample were diluted with pure water to get an appropriate concentration for the light scattering experiment and then poured into a cuvette (1 × 1 × 5 cm) using a Millipore filter of 5-μm pore size. The cuvette was set inside a sample holder made of copper which was equipped with a thermoelectric device. The temperature of the holder was maintained at a desired temperature between 20 and 50 °C, using an electronic feedback controller. The source of incident light was an argon ion laser operated at 0.5145 μm and intensity around 200 mW. The light scattered by the submicron gel beads was detected with a photomultiplier (PMT) at a scattering angle of 22°. The intensity of the scattered light fluctuates due to the Brownian motion of the submicron gel beads. The signal from the PMT was digitized via an amplifier-discriminator and was fed into a correlator. The digital 4 bits × 48 channel photon correlator (Nicomp Instruments) accumulated the time correlation function of the intensity of the scattered light. The time correlation function was fitted by use of the method of cumulants.[15] From the fits we obtained the average diffusion coefficient and, using the Stokes–Einstein relation, the hydrodynamic radius R_h.

Results and Discussion

The average hydrodynamic radius of submicron gel beads having different ionizations were 0.4071 (0), 0.4400 (8), 0.4100 (16), and 0.4400 μm (32 mM) at 22 °C, and 0.1621 (0), 0.1500 μm (8), 0.1300 (16), and 0.1000 μm (32 mM) in the collapsed state. Figure 1 shows the plots of the temperature dependence of the volume swelling ratio V/V^* of submicron gel beads, calculated from the hydrodynamic radius measured by PCS, where V^* is the gel volume at the collapsed state. The transition temperature increased with the incorporation of ionic groups into the gels. Also, gel volume is the swollen state increased with the concentration of ionic groups that contribute to osmotic pressure of counterions.

These results are consistent with the bulk properties of ionic IPA gels, which are shown in Figure 2. In the figure the swelling curves of IPA gels with different compositions are plotted as a function of temperature. The data were determined by Hirotsu, Hirokawa, and Tanaka.[4] There is a marked difference between the submicron and bulk gels: ionic submicron gels did not show a discontinuous transition, while bulk gels did. Although we do not have a clear explanation for this discrepancy, the following may account for it. One is the case that each gel bead has a different transition temperature. In this case, even if each gel bead has a discontinuous transition, the average hydrodynamic radius as measured by PCS will appear smooth and continuous. The difference of transition temperature may result from the variety of the ionic group density, cross-linkage, gel size, gel shape, etc., from bead to bead. Another explanation is possible for this continuous transition for ionic submicron gel beads, where individual submicron gel beads may undergo continuous transitions. It is known that the gel structure is affected by the substrate on which the gelation takes place. For example, the gels made on glass and plastics show different phase behavior in the portion close to the boundaries. Such surface modification will be most extensive for smaller gels because of larger surface to volume ratio. The ionic composition may be different for the surface and for the core of such gel beads. In these gels the transition temperature may be different for different radial points, and therefore, the effective radius may change gradually in response to a change in temperature.

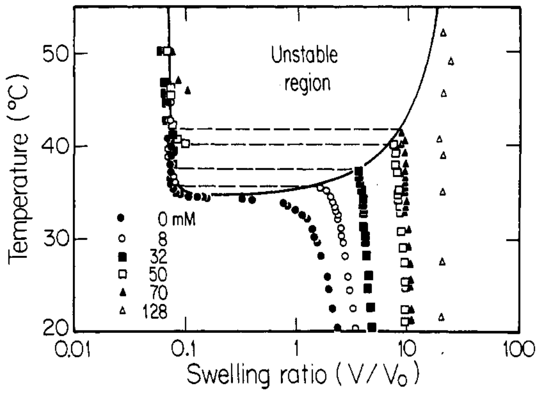

Figure 2. Equilibrium swelling ratio V/V_0 of *N*-isopropylacrylamide cylindrical gels plotted against temperature. The data are taken from ref 4. Ionic groups are introduced by copolymerization with sodium acrylate. V_0 represents the volume of gels at gelation.

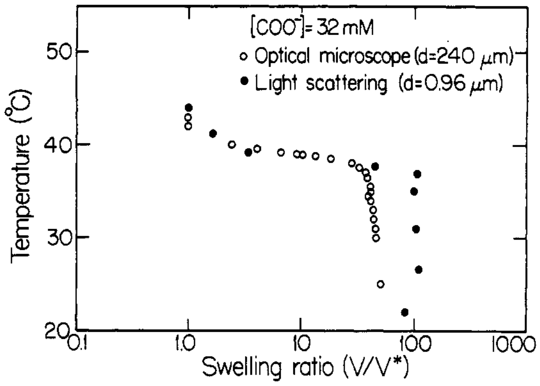

Figure 3. Equilibrium swelling ratio V/V^* of ionized *N*-isopropylacrylamide (32 mM) submicron gel beads (solid circle) and a submillimeter gel bead (open circle) plotted against temperature, where V^* is the collapsed volume. For submicron gel beads, the average size is measured by photon correlation spectroscopy. For a submillimeter gel bead the size is measured under an optical microscope. Both gel beads are found in the same batch of inverse emulsion polymerization.

To test these hypotheses, we examined the larger gel beads under an optical microscope equipped with a temperature control system. These beads were contained in the same solution where we prepared the sample for PCS measurement. The smallest size of the gel beads that we could measure under an optical microscope was 17 μm in diameter in the swollen state. All the gel beads observed showed continuous transition (Figure 3). Therefore, of the two explanations mentioned above, the latter, structural inhomogeneities within each gel bead, seems to provide a better explanation. Since gel beads with radii of the order of 20 μm or larger made by another method[11] show a discontinuous volume transition, this difference is due to the difference in the methods of bead preparation. It will be interesting to investigate quantitatively the inhomogeneities within the gels.

There are several important points to mention concerning the measurement of the size of gel beads using the technique of the PCS. The first is the polydispersity of size distribution. A monodisperse sample gives a single-exponential time correlation function. The time correlation function of a polydisperse sample departs from the single-exponential curve. Our sample was polydisperse. The result of the cumulant analysis showed about 50% for $\langle(\mathrm{D}-\langle\mathrm{D}\rangle)^2\rangle^{1/2}/\langle D\rangle$, where D is the diffusion constant and the broken brackets represent a z average.[16] From this small value of variance the ordinary cumulant analysis was appropriate and provided constant and reproducible results.

The second important point is on the internal modes of polymer density fluctuations. Even a transparent gel scatters light because of fluctuations of polymer network density in a solvent. This is light scattering by internal collective modes in gels.[1] When the gel size becomes comparable to the wavelength of the scattering vector, we way observe scattering due to internal modes in addition to light scattered from the concentration fluctuations due to translational Brownian motion of gel beads. The time correlation function of internal modes has been described by collective diffusion with a diffusion constant D_{int}.[10] Because the D_{int} is 2 orders of magnitude larger than D, we can ignore the contribution from internal modes, when D is measured by a time correlation function.

It is important to note that the static intensity of scattered light showed a marked increase at the gel collapse. This may be partly due to the change in the scattering form factor upon size decrease and partly because of aggregation of the beads. Usually at a fixed scattering angle, the scattered light intensity monotonically decreases with size because of destructive interference of light scattered from different positions within a scattering particle. It is clearly desirable to carry out classical light scattering measurement to determine the size and form factor of the aggregate, though we were not able to do so at the time of the present work.

Conclusion

The results presented in this paper support that the concept that the phase transition of ionized polymer gels holds for any size of gels as small as 1 μm. This is another example establishing the universality of the phase transition of ionic gels. There is a difference, however, between macroscopic gels and submicron gels; that is, the phase transition of the former is discontinuous, whereas the latter shows a continuous phase transition. This may be due to structural inhomogeneities within the submicron gel beads created by the interaction with surrounding solvent of surfactants during the gelation process. It will be important to prepare and study homogeneous submicron gel beads which should show discontinuous volume phase transition. It will also be of interest to examine the kinetic properties of the submicron gels using such techniques as stopped-flow measurements.

Acknowledgment. This work was supported by Toyota Central Research & Development Laboratories, Inc., and the National Science Foundation (DMR 83-10522).

Registry No. Bis(AOSI)(IPA) (copolymer), 107985-30-8.

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