Volume Phase Transition of Swollen Gels: Discontinuous or Continuous?

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAM) linear chains and spherical microgels were studied using laser light scattering. The volume change associated with the temperature dependence of the hydrodynamic radii of both the linear chains and the spherical microgels is continuous, in contrast to a discontinuous volume phase transition observed for a bulk PNIPAM gel with an identical composition. A reexamination of the volume phase transition theory shows that the phase transition temperature depends on the length of the subchain between two neighboring cross-linking points inside the gel. A comparison of the results of the linear chains and the spherical microgels suggests that the volume change of a polymer gel should be practically continuous because the inhomogeneity of the subchain length smears the volume phase transition. A possible explanation is also presented to rationalize the discontinuous volume phase transition observed in certain bulk PNIPAM gels, which is based on the bulk shear module of the gel and the microscopically inhomogeneous shrinking generated inside the gel in the volume phase transition.

Introduction

The swelling (or shrinking) of polymer gels is a fundamental and classic problem in polymer physics. A three-dimensional cross-linked polymer network filled with small solvent molecules in its interstitial space provides a model system for the study of a viscoelastic body. In addition to its importance in science, the swelling/shrinking of polymer gels under various experimental conditions, such as temperature, pH, solvent, and ion strength, has many direct applications, e.g., in a controlled drug releasing device or a chemical transducer. Flory,[1,2] Hermans,[3] and James-Guth[4] have presented several models to calculate the free energy change related to the swelling or shrinking of a polymer gel. On the basis of these models, Dusek et al.[5,6] have shown that certain polymer gels undergo a discontinuous volume change (i.e., a volume phase transition) as temperature changes by considering the chemical potential of the solvent in equilibrium with the swollen gel,

$$\Delta\mu_1/RT = \ln a_1 = \ln(1-\varphi_2) + \varphi_2 + \chi_T\varphi_2^2 + \zeta(\varphi_2^{1/3}\langle\alpha^2\rangle_0 - \kappa\varphi_2) \quad (1)$$

and the chemical potential $\Delta\mu_2/n$ per equivalent segment of the network polymer,

$$\Delta\mu_2/nRT = -\varphi_1 + \chi_T\varphi_1^2 + \zeta[\langle\alpha^2\rangle_0(\varphi_2^{-2/3}/2 + \varphi_2^{1/3} - 3/2) + \kappa(\ln\varphi_2 + \varphi_1)] \quad (2)$$

where the subscripts 1 and 2 denote the solvent and the polymer, respectively; $n = V_2/V_1$ with V being the partial molar volume; φ is the volume fraction; χ_T is the Flory−Huggins polymer−solvent interaction parameter depending on the temperature T; $\zeta = \rho V_1/M_c$, where ρ and M_c are respectively the density of the dry gel and the average molecular weight of the subchain between two neighbor cross-linking points. $\langle\alpha^2\rangle_0$ is the isotropic deformation factor of the gel network and is defined as the ratio of the mean-square end-to-end distance of the chains in a dry network to the value of unperturbed free chains; and depending on the models,[2−4] $0 < \kappa < 1$.

When two phases of different concentrations coexist, the two equations $\mu_1 = \mu_1'$ and $\mu_2 = \mu_2'$ have a solution outside the unstable region wherein $\partial\Delta\mu_2/\partial\varphi_2 > \partial\Delta\mu_1/\partial\varphi_2$. Inserting eqs 1 and 2 into $\mu_1 = \mu_1'$ and $\mu_2 = \mu_2'$, one can calculate the curves describing the composition of the gel, namely, χ_T versus φ_2. The coexistence of the swollen and the collapsed phases requires that χ_T is sufficiently high, and at the same time $\langle\alpha^2\rangle_0$ and M_c are sufficiently low. However, a low M_c means a high cross-linking density or a high $\langle\alpha^2\rangle_0$. Therefore, it is more practical to choose a gel system with a strong interaction between the polymer network and solvent, i.e., a higher χ_T, to study the volume phase transition.

This rational prediction has stimulated considerable efforts to study the volume phase transition of a pure binary polymer/solvent gel system where hydrogels are normally chosen because of their higher χ_T values. A number of studies[7−12] on certain lightly cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) gels have shown a very sharp volume change at ~33 °C which has been considered as a discontinuous volume phase transition. However, a continuous volume change has also been observed for the PNIPAM and other hydrogels.[13−17] It is worth noting that Li and Tanaka[13] have shown that, when the cross-linking density of a bulk PNIPAM gel was decreased, the continuous volume change became a discontinuous one. On the basis of eqs 1 and 2, a discontinuous volume phase transition should exist as long as the two equations $\mu_1 = \mu_1'$ and $\mu_2 = \mu_2'$ have a solution outside the unstable region.

Microscopically, there is an analogy between the “coil-to-globule” transition of a single linear polymer chain and the volume phase transition of a swollen polymer gel. The swelling or shrinking of a polymer gel is caused by the expansion or contraction of the subchains between two neighboring cross-linking points inside the gel network. Therefore, a comparison study of the coil-to-globule transition of a single linear polymer chain and a cross-linked polymer gel can lead to a better understanding of the swelling/shrinking of polymer gels.

In this study, the temperature dependence of the hydrodynamic radii of specially prepared PNIPAM high molecular weight linear chains and spherical microgels

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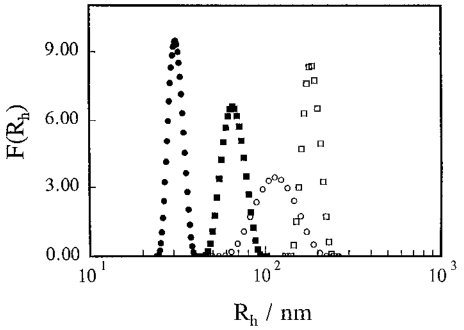

Figure 1. Hydrodynamic radius distributions $F(R_h)$ of the PNIPAM linear chains (circles) and the spherical microgels (squares) in the swollen (hollow symbols) and collapsed (filled symbols) states.

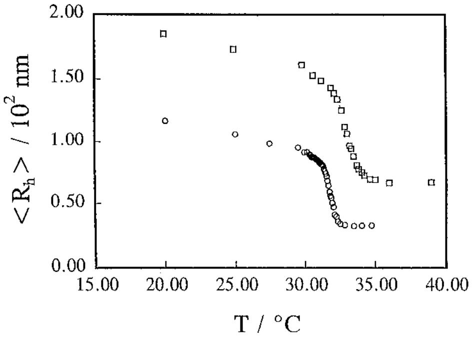

Figure 2. Temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the PNIPAM linear chain (○) and spherical microgel (□).

was investigated by dynamic laser light scattering (LLS). The details of dynamic LLS can be found elsewhere.[18] The preparation of the narrowly distributed high molecular weight PNIPAM linear chains ($M_w = 1.08 \times 10^7$ and $M_w/M_n < 1.06$) has been reported.[19] The narrowly distributed spherical microgels were prepared by emulsion polymerization, which is outlined as follows: NIPAM (3.84 g), 73.0 mg of BIS (*N*,*N*′-methylenebis(acrylamide)), 62.9 mg of SDS, and 240 mL of deionized water were mixed in a 500-mL reactor fitted with a glass stirring rod, a Teflon paddle, a reflux condenser, and a nitrogen bubbling tube. The solution was heated to 70 °C and stirred at 200 rpm for 40 min under nitrogen. Finally, 0.1536 g of KPS (potassium persulfate) dissolved in 25 mL of deionized water was added to start the reaction. The reaction was carried out for ~5 h. The microgels were purified and diluted to $\sim 1 \times 10^{-5}$ to $\sim 1 \times 10^{-6}$ g/mL for the LLS measurements.

Results and Discussion

Figure 1 shows a clear shrinking of the linear chains and spherical microgels when temperature increases, demonstrating an expected lower critical solution temperature (LCST). Both the linear chains and the spherical microgels are narrowly distributed with a variance of ~0.01. The slightly broader distribution of the linear chains in the swollen state can be attributed to the additional conformation distribution.[20] Figure 2 shows that the average hydrodynamic radius, $\langle R_h \rangle$, decreases 3−4 times when T increases from 20 to 36 °C, where $\langle R_h \rangle = \int_0^\infty F(R_h) R_h \, \mathrm{d}R_h$. The shrinking of the linear chains and spherical microgels can be better viewed in terms of the reduced hydrodynamic volume change, V/V^*, as shown in Figure 3.

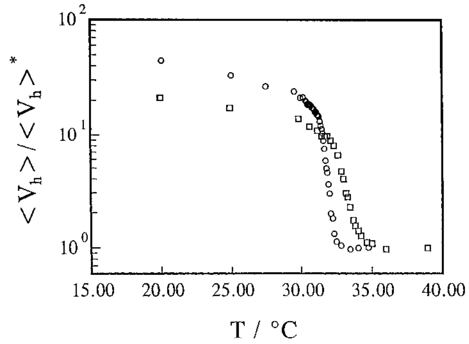

Figure 3. Temperature dependence of the swelling ratio $\langle V_h \rangle / \langle V_h \rangle^*$ of the PNIPAM linear chain (○) and spherical microgel (□) in deionized water. $\langle V_h \rangle^*$ is the average hydrodynamic volume at the collapsing limit.

At 20 °C, the swelling of the microgels is much less than the swelling of the linear chains because of the cross-linking inside the microgels. In both of these cases, the volume changes are continuous. It is well-known that for a linear polymer chain in solution its phase transition temperature varies with its molecular weight.[1] For a given polymer solution with an LCST, the higher the molecular weight, the lower the phase transition temperature. Therefore, for a polydisperse sample, polymer chains with different lengths undergo the phase transition at different temperatures. Thus, smearing of the discontinuous phase transition occurs so that the phase transition of the linear PNIPAM chains becomes continuous (Figure 3). We believe that the volume phase transition observed in this study is much sharper but remains continuous compared to previously reported results because a much more narrowly distributed PNIPAM sample was used in this study.[19] It is expected that a monodisperse polymer chain will display a discontinuous phase transition. It should be noted that Grosberg et al.[21] recently predicted the $(C/a^6)^{1/2}$ dependence of the sharpness of the coil-to-globule transition, namely, if $(C/a^6)^{1/2}$ is smaller than 0.05, the transition will be first order (sharp); and if $(C/a^6)^{1/2}$ is larger than 0.05, the transition will be second order (smooth), where C is the third virial coefficient and a is the statistical segment of the chain. Our previous study showed that even at 20 °C, which is far away from the Flory Θ-temperature (~30.59 °C), the value of A_2 is only on the order of 10^{-5} and the value of C is practically 0. It is expected that when the coil-to-globule transition temperature (practically from 30.8 to 31.8 °C) is very close to the Θ-temperature, the value of C will be even smaller. Therefore, the ratio of $(C/a^6)^{1/2}$ must be very small, which is supported by a comparison of Figure 3 with the theoretical prediction (Figure 7 in ref 20).

Figure 3 shows that the linear chains have a sharper volume change and a lower transition temperature than the microgels. Tanaka et al.[7] have attributed this less sharp volume change to the microgel's polydispersity. However, according to eqs 1 and 2, the phase transition temperature (equivalently χ_T) is not related to the gel dimension because temperature is a thermodynamic intensive property. In contrast, χ_T or the phase transition temperature is directly related to the subchain length or M_c.

Figure 4 shows a simulation of χ_T versus φ based on eqs 1 and 2 whereby χ_T decreases as ζ decreases, i.e., as M_c decreases. Note that for a polymer gel with an LCST a higher χ_T means a higher temperature. Therefore, the transition temperature decreases as M_c increases. On the basis of this M_c dependence of χ_T, it becomes clear that the linear chains have a lower transition temperature because of their much higher

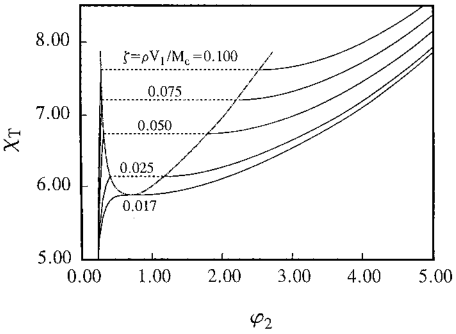

Figure 4. Plot of χ_T versus φ_2 for a polymer gel based on eqs 1 and 2, wherein we have chosen $\kappa = 0.5$, $\langle\alpha^2\rangle_0 = 0.04$, and $\zeta = \rho V_1/M_c$ (see eqs 1 and 2).

average molecular weight ($M_w = 1.08 \times 10^7$) compared to the subchains ($M_c \sim 10^4$) inside the microgels.

Normally, the subchains inside a polymer gel have a broad molecular weight (length) distribution and a gel network can be visualized as a set of subnetworks, with each subnetwork having a different M_c. As temperature changes, the subnetwork with a longer subchain will undergo the phase transition before the subnetwork with a shorter subchain. Thus, different parts of the gel network undergo the phase transition at different temperatures. The fact that a transparent PNIPAM gel changes into a milky gel in the phase transition indicates this microscopic inhomogeneity. Therefore, the volume phase transition of a polymer gel should be practically continuous because the subchains normally have a broad chain length distribution. Moreover, using this subchain inhomogeneity it is also possible to explain that because of a higher homogeneity gels with a lower cross-linking density display a discontinuous volume phase transition. However, the real picture is expected to be more complicated than described, but the essence of the physics remains.

Conceptually, the discontinuous volume phase transition predicted on the basis of eqs 1 and 2 is correct if M_c is a constant. In other words, the subchains have a uniform chain length. However, it will be extremely difficult, if not impossible, to prepare such a polymer gel. However, it should be noted that the use of one average M_c in eqs 1 and 2 has been very successful in many other predictions, e.g., in the relation between a shear modulus G and M_c, i.e., $G = RT\rho\phi/M_c$, where ϕ is the volume ratio of the dry and swollen gels.

For a discontinuous volume phase transition observed in bulk PNIPAM gels, a possible explanation is as follows. As discussed earlier, longer subchains inside the gel undergo the phase transition before shorter subchains. Therefore, the shrinking of a small amount of longer subchains initially will not alter the overall dimension of a bulk gel because of its shear modulus, but can build up stress inside the gel. When temperature increases, the stress will gradually increase until the shear modulus cannot maintain the macroscopic shape of the gel and the overall dimension of the gel will change abruptly, i.e., a discontinuous macroscopic volume change. As for the microgels with an average radius of ~0.1−0.2 μm, the shear modulus plays a minor role so that its dimension changes continuously when the stress increases. It is known[22] that a very long time (a few days) is needed for a bulk gel to reach its true swelling or shrinking equilibrium. For such a long time period, the temperature has to be kept constant (e.g., ±0.01 °C in this study) and the incremental temperature change has to be less than 0.1 °C; otherwise a continuous volume phase change could be interpreted as a discontinuous one. In contrast, the study of the microgels is more straightforward because they can reach equilibrium in less than 1 s.

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