

Surfactant Effect on pH and Temperature Sensitivities of Poly(*N*-vinylcaprolactam-*co*-sodium acrylate) Microgels

Shufu Peng[†] and Chi Wu^{*,†,‡}

The Open Laboratory of Bond-selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, China, and Department of Chemistry, The Chinese University of Hong Kong

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ABSTRACT: Spherical poly(*N*-vinylcaprolactam-*co*-sodium acrylate) [P(VCL-*co*-NaA)] microgels are pH and temperature sensitive. The addition of a small amount of anionic surfactant, sodium dodecyl sulfate (SDS), can greatly alter its pH and temperature dependence. A combination of static and dynamic laser light scattering was used to study the incorporation of surfactant in the microgels and its effect on the shrinking and swelling. When both pH and temperature were fixed, the microgel swelled as more surfactant was added due to the concentration of surfactant inside the microgel. For a fixed temperature, there existed a critical pH at which the swelling reached its maximum since the addition of NaOH had two opposite effects on electrostatic repulsion, namely, ionizing the COOH group and increasing the ionic strength. The maximum shifted to a lower pH when more surfactant was added. For a fixed pH, the microgel shrank when the temperature rose. The shrinking temperature became high when the surfactant concentration or pH increased. In comparison with various chemical modifications of a similar system, the incorporation of a small amount of surfactant into the microgel provided a convenient way to vary its critical shrinking temperature and pH for different applications.

Introduction

Poly(*N*-vinylcaprolactam) (PVCL) as a thermally sensitive water-soluble polymer is biocompatible. The hydrogels made of PVCL have a volume transition temperature around the body temperature.^{1–3} So far, only few studies related to its properties and applications have been publicly reported even though PVCL has been commercially available for a long time from BASF.^{4–6} Recently, thermally sensitive polymer gels have attracted much attention because of their potential chemical and biomedical applications. To develop a gel for a particular application, it is often necessary to chemically modify the gel network by incorporating different hydrophobic or hydrophilic groups in the chain backbone to shift its normal swelling/shrinking temperature or pH to a desired one.

The swelling and shrinking of a polymeric gel network can be generally attributed to a balance between the repulsion and attraction among functional groups attached to the gel network. These repulsions and attractions can arise from a combination of four intermolecular forces: namely, electrostatic, hydrophobic, van der Waals, and hydrogen bonding.⁷ When a repulsive force, usually electrostatic in nature, overcomes an attractive force such as hydrogen bonding or hydrophobic interaction, the gel network swells, sometimes “discontinuously” leading to a volume transition.⁸ The variables that can trigger and shift the swelling and shrinking depend on the nature of intermolecular forces existing in the gel network.⁹ One can chemically introduce charged groups to a hydrophobic gel network, either via hydrolysis or copolymerization with ionic comonomers, to alter its swelling behavior in water and make it sensitive to the ionic strength and pH.^{10,11}

The interaction between polyelectrolytes and surfactant has been an interesting subject for a long time in both fundamental and technological research.^{12–16} The studies of the interaction between a polyelectrolytes gel network and surfactant have revealed three different controlling effects:^{17–21} the translational entropy of counterions and electrostatic and hydrophobic interactions. It has been shown that the surfactant can form micelles in polymer gels even at a concentration much lower than its critical micelle concentration.^{16,22} This leads to a possibility of using surfactant to change the swelling/shrinking behavior of a thermally sensitive polymer gel instead of a more complicated chemical modification. In this study, small microgels poly(*N*-vinylcaprolactam-*co*-sodium acrylate) (~200 nm) were used to study the surfactant effect on their pH and temperature sensitivities. There are several advantages of using small microgels over using a bulk gel. For example, the equilibrium can be reached in minutes instead of in days, and the swelling and shrinking can be monitored by an accurate laser light scattering spectrometer instead of by eyes or a CCD camera.

Experimental Section

Microgel Preparation. *N*-Vinylcaprolactam monomer (VCL, courtesy of BASF) was purified by vacuum distillation. Sodium acrylate comonomer (NaA, Lancaster) and surfactant sodium dodecyl sulfate (SDS, Aldrich) were used without further purification. Potassium persulfate as an initiator (KPS, Aldrich) and *N,N*-methylenebis(acrylamide) as a cross-linking agent (MBAA, Aldrich) were recrystallized three times in methanol. Sodium hydroxide (anhydrous NaOH, ACROS) and hydrochloric acid (0.1 N HCl standard solution, BDH) were used to adjust pH which was measured by a pH-meter (pH 3C-H, Shanghai Leici Ins.). Poly(*N*-vinylcaprolactam-*co*-sodium acrylate) [P(VCL-*co*-NaA)] microgels were prepared by precipitation polymerization in water. VCL monomer, NaA comonomer, MBAA, and deionized water were added into a three-neck flask equipped with a reflux condenser, a thermometer and a nitrogen-bubbling tube. The solution was

* To whom correspondence should be addressed.

[†] The Chinese University of Hong Kong.

[‡] University of Science and Technology of China.

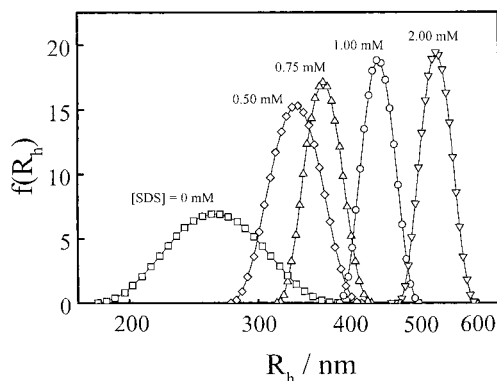


Figure 1. Surfactant concentration [SDS] dependence of hydrodynamic radius distribution $f(R_h)$ of P(VCL-*co*-NaA) microgels in water at 25 °C and pH = 6.2.

stirred and bubbled by nitrogen to remove oxygen before KPS aqueous solution was added to start the polymerization at 60 °C for 24 h. The resultant microgel was purified by a successive four cycles of centrifugation (Sigma 2K15 ultracentrifuge, at 15 300 rpm and 40 °C), decantation, and redispersion in deionized water to remove unreacted low molar mass molecules. The microgels, on average, contained 1.0 mol % acrylic groups.

Laser Light Scattering (LLS). The detail of laser light scattering instrumentation can be found elsewhere.²³ In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh factor $R_v(q)$, can lead to the weight-average molar mass (M_w), the root-mean-square z -average radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$, or written as $\langle R_g \rangle$) and the second virial coefficient (A_2), where q is the scattering vector. In dynamic LLS, the cumulant analysis or Laplace inversion of the measured intensity–intensity time correlation function $G^{(2)}(q, t)$ in the self-beating mode can result in an average line width ($\langle \Gamma \rangle$) or a line width distribution ($G(\Gamma)$).^{24,25} For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{c \rightarrow 0, q \rightarrow 0} = D$ and the hydrodynamic radius (R_h) via the Stokes–Einstein equation, $D = k_B T / (6\pi\eta R_h)$, where k_B , T , and η are the Boltzmann constant, the absolute temperature and the solvent viscosity, respectively.²⁶

Results and Discussion

Figure 1 shows that when both pH and temperature are fixed, the microgels swell when more surfactant is added. Note that here the surfactant molar concentration [SDS] is well below its critical micelle concentration (cmc \sim 8.0 mM). It is known that SDS can form micelles in the gel network,^{22,27} so that electrostatic repulsion between the anionic group (COO⁻) on the gel network and anionic surfactant leads to the swelling.^{28,29} Figure 2 shows that the average hydrodynamic radius $\langle R_h \rangle$ increases with [SDS]. This indicates a concentration of SDS inside the microgels, which can be better viewed in terms of the change of the average number (n_s) of surfactant molecules inside each microgel. n_s can be determined from the increase of the apparent average weight molar mass ($M_{w,app}$) of the microgels; namely, $n_s = (M_{w,app} - M_{w,gel}) / M_{surfactant}$, where $M_{w,gel}$ is the average molar mass of the microgels in the absence of surfactant and $M_{surfactant}$ is the molar mass of surfactant. Figure 2 shows that when both pH and temperature are fixed, n_s does increase when more surfactant is added.

It is known that for two like charged groups separated by a distance (r), the electrostatic repulsion force (f) is reciprocally proportional to r^2 , i.e., $f \propto r^{-2}$. Note that r decreases as n_s increases by $r \propto n_s^{-1/3}$, so that $f \propto n_s^{2/3}$. On the other hand, the swelling deformation is linearly

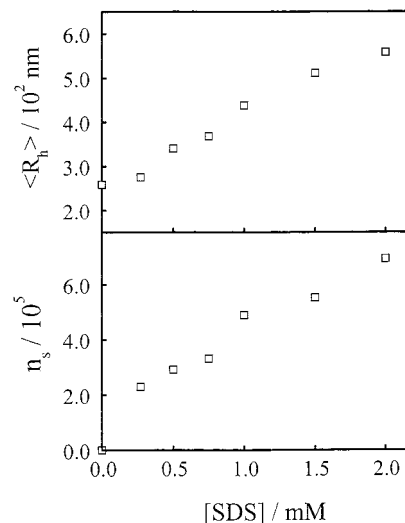


Figure 2. Surfactant concentration [SDS] dependence of average hydrodynamic radius $\langle R_h \rangle$ of P(VCL-*co*-NaA) microgels and average number (n_s) of surfactant molecules concentrated inside each microgel at 25 °C and pH = 6.2.

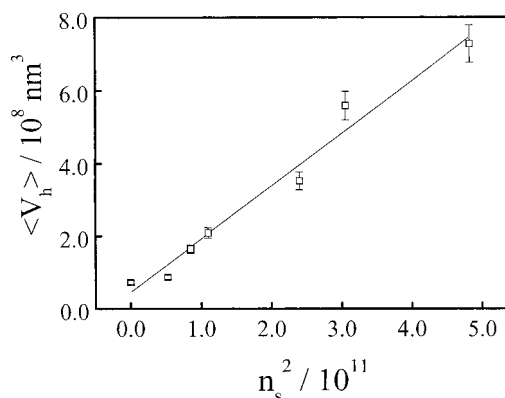


Figure 3. Plot of average hydrodynamic volume $\langle V_h \rangle$ of P(VCL-*co*-NaA) microgels vs the square of the average number (n_s) of surfactant molecules concentrated inside each microgel at 25 °C and pH = 6.2, where $\langle V_h \rangle = (4\pi/3)\langle R_h \rangle^3$.

proportional to the repulsion force. Therefore, $\langle R_h \rangle \propto n_s^{2/3}$, which is exactly what we have observed in Figure 3, where $\langle V_h \rangle = (4\pi/3)\langle R_h \rangle^3$. Figure 3 clearly reveals, for the first time, that the surfactant-induced swelling can be attributed to the electrostatic repulsion between the anionic surfactant molecules concentrated inside the microgel network.

Figure 4 shows that, for a given temperature, the swelling of the microgels as pH increases in the lower pH range is limited. There exists a critical pH at which $\langle R_h \rangle$ rapidly increases to a maximum. Further increase of pH leads to shrinking. The critical pH decreases as [SDS] increases. This is because the binding of SDS to the PVCL chains through hydrophobic interaction converts the microgel into polyelectrolytes. It is these additional charges and their counterions that exert an extra osmotic pressure on the gel network. It is clear that when pH is low, the effect of SDS on the swelling is more profound. It is known that at a lower pH, most of the carboxylic groups are in the acid form (–COOH) and the gel network becomes neutral. The swelling is attributed to the concentration of SDS inside the microgel. As pH increases, more and more carboxylic groups become anionic –COO⁻ groups so that the microgel swells even in the absence of SDS. We found that the microgels copolymerized with 1.0 mol % sodium

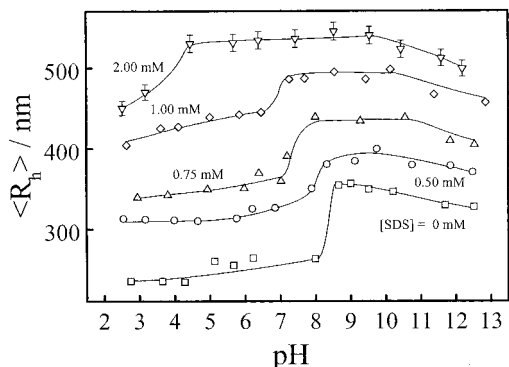


Figure 4. pH dependence of average hydrodynamic radius ($\langle R_h \rangle$) of P(VCL-co-NaA) microgels in the presence of different amounts of surfactant SDS at 25 °C.

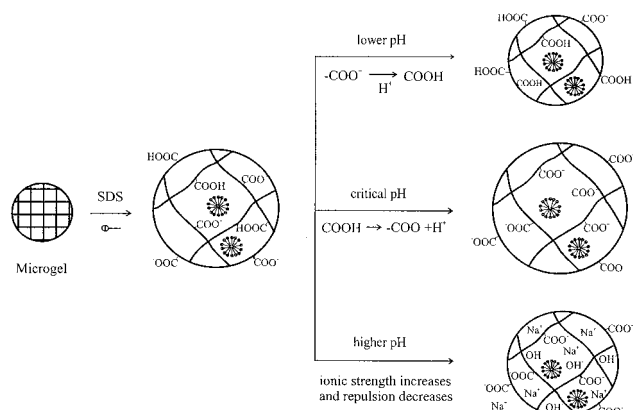


Figure 5. Schematic of the electrostatic interaction between P(VCL-co-NaA) microgel network and anionic surfactant SDS and the effect of pH on the swelling.

acrylate in the presence of 0.5, 0.75, 1.0, and 2.0 mM SDS have a similar pH dependence as those copolymerized with 3.6, 5.3, 7.1, and 14.2 mol % of sodium acrylate in the absence of SDS, respectively.

The effects of adding surfactant and NaOH are schematically shown in Figure 5. The anionic surfactant concentrated inside the microgel increases the electrostatic repulsion and makes the microgel swell. The addition of NaOH has two opposite effects: one is to ionize the carboxylic groups and enhance the electrostatic repulsion; and the other is to increase the ionic strength and weaken the electrostatic repulsion. When pH is low, these two effects are partially canceled with each other so that the swelling is limited. At the critical pH, all the carboxylic groups are ionized. Further addition of NaOH can only enhance the second effect, which explains the shrinking of the microgel in the high pH range.

Figure 6 shows that, for a given SDS concentration, the microgels gradually shrink when the temperature is raised. This is because the increase of temperature weakens the hydration so that the chain backbone gradually becomes more hydrophobic, but the temperature has a much smaller effect on the electrostatic repulsion, leading to the collapse of the gel network. The temperature independence of M_w indicates that there is no interparticle aggregation. It is necessary to state that the values of dn/dc are 0.232, 0.226, and 0.212 at 25, 32, and 40 °C, respectively. It is clear that increasing pH can profoundly raise the shrinking temperature. As discussed before, for a given temperature, the swelling of the microgels as [SDS] increases is due to the concentration of SDS inside the gel network.

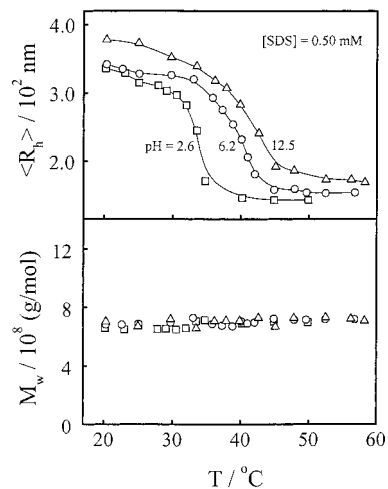


Figure 6. Temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) and weight-average molar mass (M_w) of P(VCL-co-NaA) microgels in water at a given surfactant concentration, but different pH.

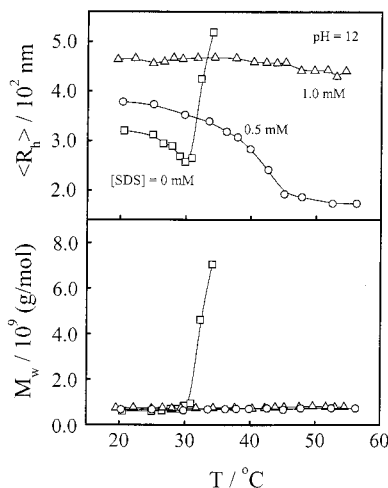


Figure 7. Temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) and weight-average molar mass (M_w) of P(VCL-co-NaA) microgels in water at a given pH, but different surfactant concentrations.

Figure 7 shows that the addition of only 0.5 mM SDS shifts the shrinking temperature to ~ 45 °C. When [SDS] is 1.0 mM, $\langle R_h \rangle$ becomes independent of the temperature, indicating that the shrinking temperature has already been shifted outside the range studied. It is interesting to see that the surfactant-free microgels aggregate at ~ 31 °C in a high pH dispersion, reflecting in a sharp increase of M_w . Note that the high ionic strength at pH = 12 weakens the electrostatic repulsion, so that the presence of an excess amount of Na^+ and OH^- has a salt-out effect on the microgels.^{10,30} Actually, the addition of NaCl instead of NaOH had a similar effect as shown in Figure 8. It has been suggested that there exist two types of water structures: Coulombic and hydrophobic, comprising the hydration sheath of polymer.³¹ It is expected that the hydrophobic hydration of P(VCL-co-NaA) would exclude Coulombically hydrated anionic surfactant, resulting in a more hydrophobic chain. This explains why the microgels in the presence of salt start to aggregate at higher temperatures.

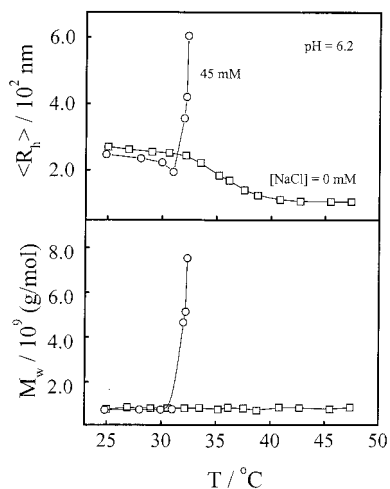


Figure 8. Temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) and weight-average molar mass (M_w) of surfactant-free P(VCL-*co*-NaA) microgels with and without the addition of NaCl.

In summary, our results demonstrate that the incorporation of a small amount of anionic surfactant sodium dodecyl sulfate in a spherical poly(*N*-vinylcaprolactam-*co*-sodium acrylate) microgel can greatly alter its pH and temperature sensitivities, leading to a similar swelling and shrinking behavior as those gels modified chemically with different amounts of ionic groups. We found that the surfactant-induced swelling is closely related to the concentration of anionic surfactant molecules inside the gel network, reflecting in an observed relation between the average hydrodynamic volume ($\langle V_h \rangle$) and the average number (n_s) of surfactant concentrated in each microgel; namely, $\langle V_h \rangle \propto n_s^2$. We have shown that using a small amount of surfactant is much simpler and cheaper than a chemical modification. The principle demonstrated in this study can be easily applied for other types of pH and thermosensitive hydrogels.

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