Phase Transition Behavior of Hydroxypropylcellulose under Interpolymer Complexation with Poly(acrylic acid)

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ABSTRACT: The phase transition behavior of hydroxypropylcellulose (HPC) under interpolymer complexation with poly(acrylic acid) (PAA) has been studied by turbidity and laser light scattering measurements. It has been found that the lower critical solution temperature (LCST) of the HPC was drastically reduced after adding 1 wt % of PAA into the HPC solution. The LCST of the HPC/PAA complexes decreased with the increase of the molecular weight of either the HPC or the PAA. The driving force shifting the LCST is attributed to the hydrogen bonding and hydrophobic interaction of the macromolecules. As the pH value increases from at 4.0 to 6.0, the LCST of the HPC−PAA complex decreases. This may be due to the salt effect of the polyelectrolyte on the nonionic polymer. The HPC/PAA complexation has been observed even at very dilute solution of 1.6×10^{-5} g/mL at pH = 3.2. The study of complexation between the HPC and the PAA leads to a new method for synthesis of surfactant-free microgels at room temperature. The resultant microgels swell and collapse at the pH value higher and lower than the pK_α value of the PAA, respectively.

Introduction

Interpolymer complexes are physically interacted polymer chains in solution and have been extensively investigated.[1−4] The formation of polymer complexes between a proton-accepting polymer such as poly(ethylene oxide) (PEO) and a proton-donating polymer such as poly(acrylic acid) (PAA) via H-bonding in aqueous media has attracted a continuing interest as a model of biological systems.[5−9] The complexation of different polymers in solution is a commonly used procedure for tailoring polymer properties to specific needs without chemical modification of these macromolecules. Most studies have been performed on the polymer complex systems, mainly focusing on the factors that affect complexation, including stoichiometric ratio of two complementary polymers, pH, ionic strength, solvent, concentration, and structure of the component polymers.[10−12]

However, only a few studies[13,14] have been reported so far on the effect of complexation on the lower critical solution temperature (LCST) of a nonionic polymer. Hence, for a model study, we have chosen the hydroxypropylcellulose (HPC) as a proton-accepting polymer and poly(acrylic acid) (PAA) as a proton-donating polymer to study how the complexation between these two polymers affect the LCST of the HPC polymer under various conditions. Our literature survey shows that studies of the structure and properties of interpolymer complexes between poly(acrylic acid) and nonionic cellulose ethers have been reported.[15−23] Specifically, Budtova and co-workers[15−17] investigated the formation and properties of the interpolymer complexation between PAA and cellulose ethers including hydroxyethylcellulose (HEC) and methylcellulose (MC). Their experimental results showed that the mixtures of the cellulose ethers and nonionized PAA in aqueous solution formed interpolymer complexes due to hydrogen bonding. However, to our knowledge, systematic studies of the phase transition behavior of the HPC/PAA complex with change of pH have not been reported.

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The HPC exhibits a lower critical solution temperature (LCST) at 41 °C and a remarkable hydration−dehydration change in aqueous solution in response to relatively small changes in temperate around the LCST.[24,25] Below the LCST, the HPC chains hydrate to form an expanded structure; above the LCST, the HPC chains dehydrate to form a shrunken structure. This property is due to the reversible formation and cleavage of the hydrogen bonds between the HPC and surrounding water molecules with changing temperature. The swelling behaviors of the HPC bulk gels, microgels, and polymer chains have been previously reported.[24−27] The advantage of the HPC over many other synthetic thermally responsive macromolecules is that the HPC is one of the cellulose ethers approved by the United States Food and Drug Administration for the use in food, drug, and cosmetics,[28−30] whereas many synthetic macromolecules are produced from carcinogenic and teratogenic monomers.

It is well-known that incorporating hydrophobic comonomers leads to a lower LCST, while incorporating hydrophilic comonomers leads to a higher LCST. The changes in LCST caused by incorporating comonomers are due to changes in the overall hydrophilic properties of the polymer. This effect has been investigated for another important thermally responsive polymer *N*-isopropylacrylamide (NIPA).[31]

Here we show that, based on complexation between the HPC and the PAA, the LCST of HPC can be drastically changed. The phase transition behavior of the HPC/PAA complex has been correlated with polymer concentration, temperature, pH, and macromolecular weight using turbidity and dynamic laser light scattering measurements. We further demonstrate that the complexation between HPC and PAA leads to a new method for the formation of surfactant-free PAA microgels directly in aqueous media at room temperature. Such microgels have very narrow size distributions as characterized by light scattering techniques and can reversibly swell and shrink in response to external stimuli such as pH. These microgels may be used as building blocks for the formation of nanoparticle networks[32] or carriers for controlled drug delivery.

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Experimental Section

Materials. Dry hydroxypropylcellulose (HPC) powders (average $M_w = 1.0 \times 10^6$ and average $M_w = 1.0 \times 10^5$) and poly(acrylic acid) (PAA) solution (25 wt %, average $M_w = 2.4 \times 10^5$; 25 wt %, average $M_w = 9.0 \times 10^4$) were purchased from Aldrich Chemical Co.

The substitution level of the HPC samples of two molecular weights in this paper is MS = 3.9, where MS is defined as the average member of molecules of alkylene oxide combined per anhydroglucose unit.[24] Deionized and distilled water were used throughout.

Sample Preparation. The HPC powder was dissolved in dionized water by gentle stirring for 3−4 days at a concentration of 1 wt % at room temperature. The 25 wt % solution of PAA was diluted to 2.5 wt %. These two solutions were then mixed to produce the desired concentrations studied in this paper. The phosphate buffered saline was employed for preparing different pH solutions.

Turbidity Measurement. The increased insoluble polymer concentration can scatter light and reduce the transmission of visible light. The turbidity (a) is defined as the reduction in fractional light intensity per unit penetration length in the sample and is given by $a = -(1/L)\ln(I_t/I_0)$,[33] here L is the path length or the thickness of the sample, I_t is the intensity of the transmitted light, and I_0 is the intensity of the incident light. In this experiment, the turbidity was measured using a spectrophotometer (Milton Roy Ltd. Spectronic 301) at the wavelength of the incident light of 555 nm. The sample's temperature was controlled by a circulation water bath (Fisher Scientific, model 9110). The temperature of the sample was measured using a digital multimeter and a thermocouple configuration standardized at 0° C with ice. The sample was allowed 30 min or longer to reach equilibrium after each temperature adjustment.

Dynamic Light Scattering Characterization. A commercial laser light scattering (LLS) spectrometer (ALV-5000, Germany) was used with a helium−neon laser (Uniphase 1145P, output power of 22 mW, and wavelength of 632.8 nm) as the light source. The incident light was vertically polarized with respect to the scattering plane, and the light intensity was regulated with a beam attenuator. The scattered light was transmitted through a very thin (~100 μm in diameter) optical fiber connecting to an active quenched avalanche photodiode (APD), the detector. The coherent factor β in dynamic laser light scattering was about 0.98. The avalanche photodiode had sensitivity 2 orders higher than that of a normal photon multiplier (PM) tube, while its dark count increased no more than 10 times. Thus, a 22 mW laser could have a measured count rate similar to a 400 mW laser for a normal PM tube.

In dynamic LLS, the intensity−intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured and can be expressed by[34]

$$G^{(2)}(t,q) = \langle I(t,q)\, I(q,0)\rangle = \langle I(0)\rangle^2 g^{(2)}(t) = \langle I(0)\rangle^2 [1 + |g^{(1)}(t)|^2] \quad (1)$$

where t is the decay time and $q = (4\pi n/\lambda_0)\sin(\theta/2)$. $g^{(1)}(t) \equiv [\langle E(0)\, E^*(t)\rangle/\langle E(0)\, E^*(0)\rangle]$ and $g^{(2)}(t) \equiv [\langle I(0)\, I(t)\rangle/\langle I(0)\rangle^2]$ are the normalized field−field and normalized intensity−intensity autocorrelation functions, respectively. In practice, the detection area cannot be zero. Therefore, the scattered light cannot be purely coherent, and an instrument parameter, β (<1), is introduced in eq 2[34]

$$G^{(2)}(t,q) = A[1 + \beta|g^{(1)}(t)|^2] \quad (2)$$

where A ($\equiv\langle I(0)\rangle^2$) is a measured baseline and β is the coherence factor. $g^{(1)}(q,t)$ is related to the line-width distribution $G(\Gamma)$ by

$$g^{(1)}(t,q) = \langle E(t,q)\, E^*(0,q)\rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}\, d\Gamma \quad (3)$$

$G(\Gamma)$ can be obtained from the Laplace inversion of $g^{(1)}(q,t)$.

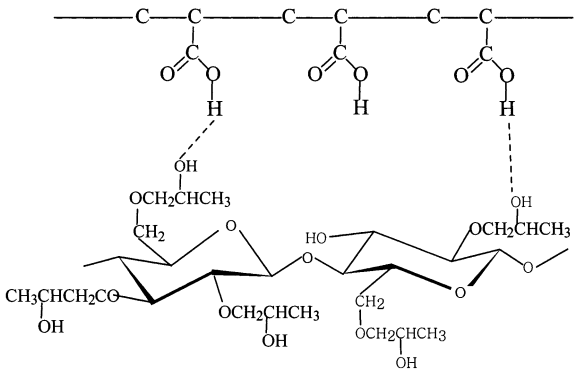

Figure 1. Schematic hydrogen bonding between the hydroxypropylcellulose (HPC) and poly(acrylic acid) (PAA).

$g^{(1)}(q,t)$ was analyzed by a cumulant analysis to get the average line width $\langle\Gamma\rangle$ and the relative distribution width $\mu_2/\langle\Gamma\rangle^2$. The extrapolation of Γ/q^2 to $q \to 0$ led to the translational diffusion coefficient (D). Further, $G(\Gamma)$ can be converted to the translational difffusion coefficient distribution $G(D)$ and to the hydrodynamic radius distribution $f(R_h)$ using the Stokes−Einstein equation.

$$R_h = \frac{k_B T}{6\pi\eta D} \quad (4)$$

where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. The dynamic light scattering experiments were performed at scattering angle $\theta = 30°$.

Results and Discussion

Effect of Polymer Concentrations and Molecular Weight on the LCST of HPC−PAA Complex. Hydroxypropylcellulose in water has the LCST at approximately 41 °C,[24,25] while poly(acrylic acid) is a hydrophilic macromolecule and readily dissolves in water. The phase transition of the HPC may be caused by the delicate hydrophilic−hydrophobic balance of HPC configuration. Each propylene oxide moiety in the HPC has two C−C bonds and two C−O bonds. At low temperatures in polar solvents, oxygen preferentially maintains a gauche orientation about C−C bonds and a trans conformation about C−O bonds. This bond configuration of the HPC has a relatively large dipole moment. When the temperature is increased, the solvating environment of water becomes less polar. The dipole moment of the propylene oxide moieties may be reduced to such an extent that the phase transition of the HPC occurs.[39]

When the HPC and the PAA are mixed, the interpolymer complex is formed at pH < pK_a (pK_a = 4.7 for acrylic acid[35]) due to hydrogen bonding between the HPC and the PAA as shown in Figure 1. That is, the PAA polymer acts as a proton donor interacting with a proton acceptor (HPC) to form an interpolymer complex.

Figure 2a shows the turbidity of the HPC−PAA complex in aqueous solution as a function of temperature at different HPC concentrations with HPC molecular weight of 1.0×10^6 at pH = 3.2. The LCST of HPC shifted to a lower temperature upon increasing the HPC concentration from 0.06 to 0.60 wt % while the PAA is kept the same at 1.0 wt %, compared to that of pure HPC solution. The decrease of the phase transition temperature is contributed to the formation of intermacromolecular chain complexes caused by hydrogen bonding between the −COOH group of the PAA and

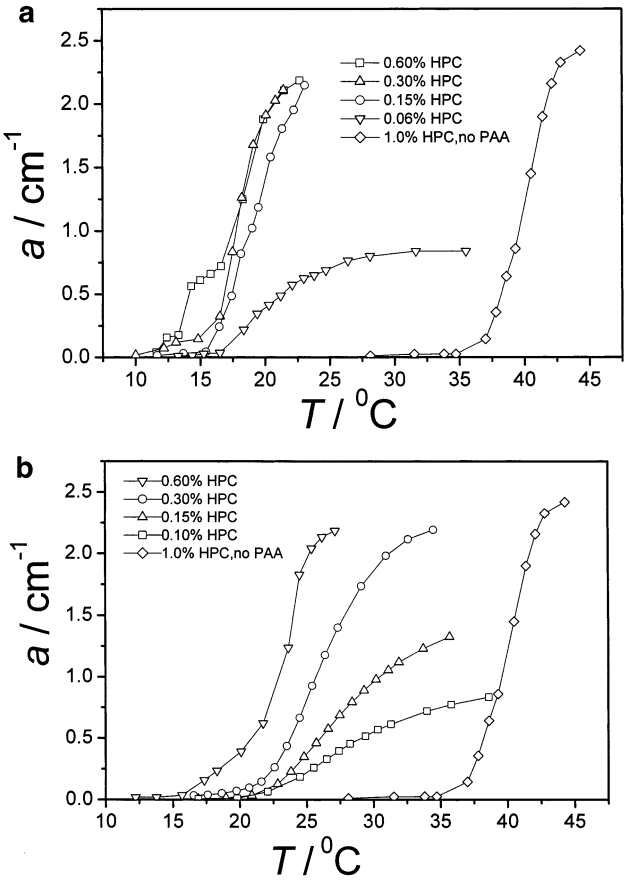

Figure 2. Temperature and HPC concentration dependent turbidity of the HPC/PAA complex at PAA concentration of 1.0 wt % at pH = 3.2 for different HPC molecular weights: (a) $M_w = 1.0 \times 10^6$, (b) $M_w = 1.0 \times 10^5$.

−OH group of the HPC. The formation of hydrogen bonds between the −COOH and −OH groups limits the accessibility of water to the HPC chains, leading to an increase in the hydrophobicity of the HPC linear macromolecules. The dipole moment of the propylene oxide moieties of the HPC linear macromolecules may be reduced to such an extent that the phase transition occurs at much lower temperature.[36] Furthermore, the onset of the phase transition of the 0.6 wt % sample is lower than that of other samples; this is due to stronger hydrophobic interaction in higher HPC concentration.

To study the effect of molecular weight on the LCST of the HPC−PAA complex, the turbidity as a function of temperature was measured for the sample with HPC molecular weight of 1.0×10^5 at pH = 3.2. Figure 2b showed that the LCSTs of HPC with lower molecular weight are higher than those of the HPC with $M_w = 1 \times 10^6$ at the same polymer concentrations. This phenomenon could be due to weaker intermolecular hydrogen-bonding interaction for the complex with lower molecular weight HPC. The HPC chains of higher molecular weight are more easily removed from the aqueous environment, resulting in a lower LCST.

Previous work has already shown that the macromolecular weight of the interacting polymer plays a very important role in forming the complexes.[4] Specifically, Morawetz et al.[37,38] studied the effect of molecular weight of the proton-accepting polymers on the complexation of PAA with poly(vinylpyrrolidone) (PVP) or poly(ethylene oxide) (PEO) using fluorescence spectroscopy. They found that the interaction of inter-macro-

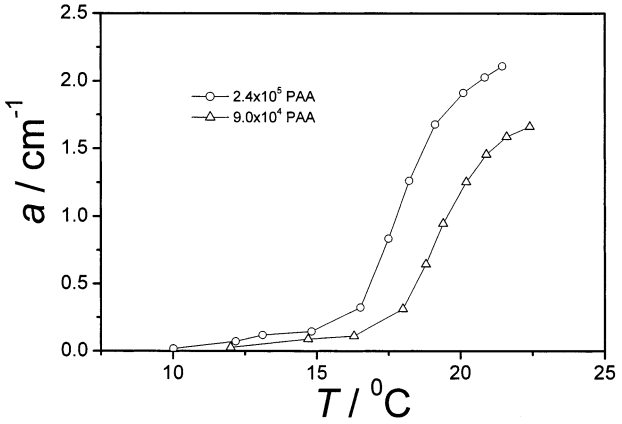

Figure 3. Comparison of turbidity of the HPC/PAA complex for two different PAA molecular weights of 9.0×10^4 and 2.4×10^5. Here the complex consists of 0.3 wt % HPC ($M_w = 1 \times 10^6$) and 1.0 wt % PAA at pH = 3.2.

molecular hydrogen bonding became stronger with the increase of the molecular weights of the proton-accepting polymers. The same mechanism may cause the decrease of the LCST of the HPC−PAA complex upon increasing the HPC molecular weight.

As a further study, we measured the turbidity of 1.3 wt % complexes (1 wt % PAA and 0.3 wt % HPC ($M_w = 1.0 \times 10^6$)) with two different PAA molecular weights of 1×10^4 and 1×10^5) at pH = 3.2. It was found that the molecular weight of the totally hydrophilic polymer PAA affects the LCST of the complexes as shown in Figure 3. The higher the PAA molecular weight, the lower the LCST, as expected.

pH Effect on the LCST of the HPC−PAA Complex. Figure 4a shows the phase transition behavior of the complexes at various pH values, and Figure 4b summarizes the LCST as a function of pH values. The data of the LCST vs pH in Figure 4b may be divided into two regions: (1) below pH = 4.0 and (2) above pH = 4.0. In the first region (pH < 4.0), poly(acrylic acid) is a weak acid and is in the molecular state at pH < pK_a (=4.7). The LCST of the complex shifts to lower temperature upon the decrease of pH. This is caused by stronger hydrogen bonding as the pH value decreases. Specially, at pH = 3.2, the LCST of the complex is 16 °C, much lower than 41 °C for the pure HPC solution. Around pH = 4.0, the phase transition behavior of the HPC−PAA complex is close to that of 1 wt % HPC solution without PAA. In the second region (pH > 4.0), it is found that the LCST decreases with the increase of the pH value. This could be caused by the salt effect of the totally ionized poly(acrylic acid).

A previous study has shown that the LCST of the nonionic HPC polymer can be shifted to a lower temperature by adding low molecular salt such as NaCl into the solution.[39] The effect of polyelectrolyte on the LCST of ionic NIPA copolymers has been reported.[40−43] To our knowledge, this is the first time that the salt effect of the ionized polyelectrolyte PAA on the LCST of the nonionic HPC has been revealed. To further demonstrate this effect, turbidity of a HPC−PAA complex with 1.0 wt % has been measured in a PBS buffered solution at pH 7.4. The results are given in Figure 5. As the PAA concentration increases, the LCST of the complex decreases. The magnitude change of the turbidity for higher PAA concentration (0.5 and 0.8 wt %) is much smaller than that of 0.2% PAA concentration.

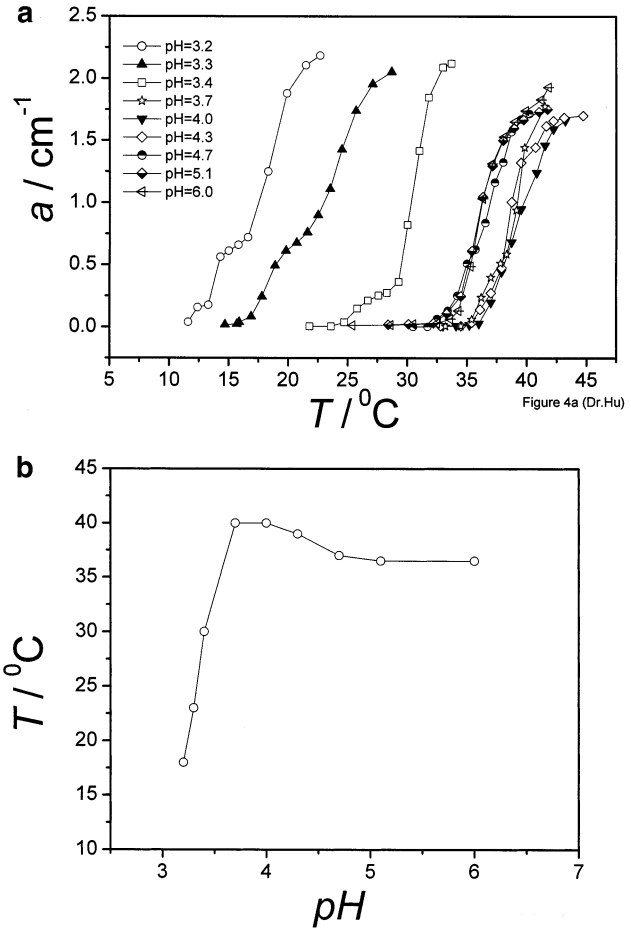

Figure 4. (a) Temperature-dependent turbidity of the HPC/PAA for different pHs at 0.6 wt % HPC and 1.0 wt % PAA. (b) The LCST of the HPC/PAA as a function of pH values.

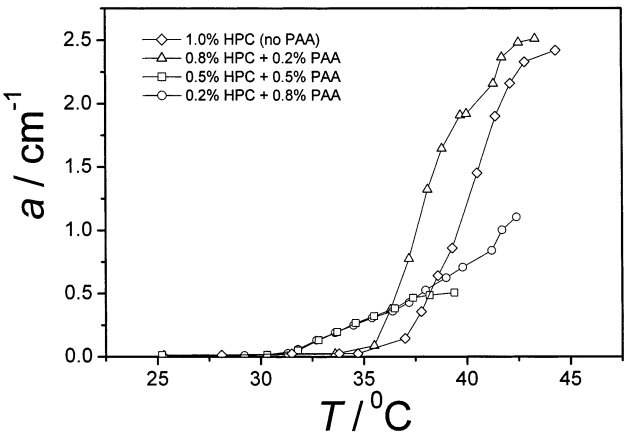

Figure 5. Temperature-dependent turbidity of the 1.0 wt % HPC/PAA at pH = 7.4 for various PAA concentrations.

Complexation in Dilute HPC/PAA Solution. The phase transition behavior of the HPC/PAA complex discussed above was studied in a relatively high polymer concentration, around 1 wt %. Here we report results of the HPC−PAA in very dilute polymer solution. As revealed by dynamic light scattering in Figure 6a, the HPC−PAA at polymer concentration of 1.6×10^{-5} g/mL can still form a complex at room temperature at pH = 3.2. It is noted that the complex has a narrowly distributed hydrodynamic radius. This narrow distribution shows that the interpolymer hydrogen bonding of the dilute HPC/PAA solutions at pH = 3.2 can cause the

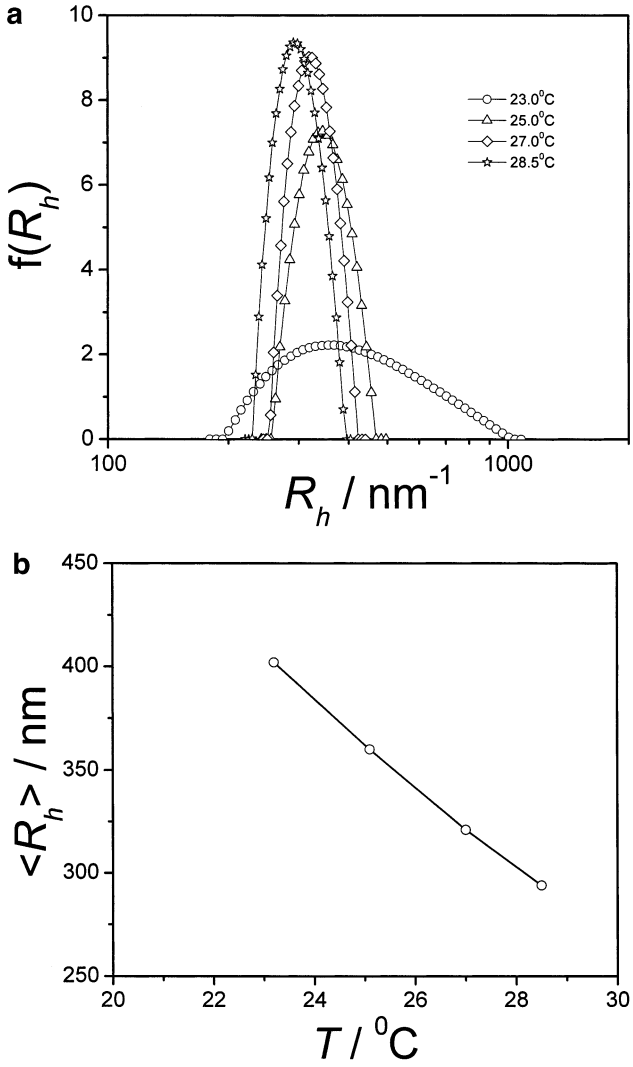

Figure 6. (a) Hydrodynamic radius distributions ($f(R_h)$) of the HPC/PAA complex nanoparticles ($C = 1.6 \times 10^{-5}$ g/mL) at pH = 3.2. (b) Average hydrodynamic radius $\langle R_h \rangle$ of the HPC/PAA complex nanoparticles at pH = 3.2 as a function of temperature.

decrease of the LCST so that they can aggregate into microgels at room temperature. In contrast, the HPC in dilute aqueous solution without PAA as a complexation agent would form nanospheres above 41 °C.[26] In addition, the hydrodynamic radius given in Figure 6b of the HPC−PAA complex in dilute polymer solution at pH = 3.2 decreases as the environmental temperature increases within the range of temperatures studied.

Surfactant-Free Synthesis of PAA Microgels Based on Interpolymer Complexation. Previously, the PAA microgels and their derivatives were synthesized using inverse microemulsion polymerization[44,45] with large amounts of organic solvent and surfactants. In practice, complete removal of the solvent and surfactants from the resultant polymeric particles is difficult, if not impossible. Here, a new method of preparing PAA microgels is proposed and demonstrated. The central idea is based on the HPC−PAA complexation in water through hydrogen bonding. At the beginning of polymerization, the PAA chains form a complex with the HPC chains at low pH values. Then the PAA can aggregate around the complexes to form microgels.

To demonstrate this idea, we have prepared PAA microgels by mixing 2.0 g of 99 wt % acrylic acid (AA),

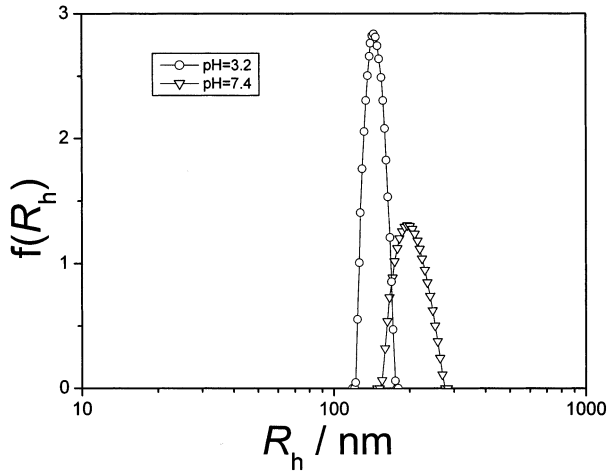

Figure 7. Hydrodynamic radius distribution ($f(R_h)$) of PAA microgel particles ($C = 1.32 \times 10^{-5}$ g/mL) synthesized based on HPC/PAA complexation with HPC/PAA concentration of 1.2×10^{-5} g/mL in pH = 3.2 and pH = 7.4 at 25 °C.

10 g of 1% HPC, and *N*,*N*′-methylenebisacrylamide as a cross-linker in 68 g of distilled and deionized water. The solution was stirred at 26 °C under nitrogen for 50 min. Then, 50 mg of ammonium persulfate in 10 g deionized water and 50 mg of tetramethylethylenediamine (TEMED) in 10 g deionized water were added into the solution to initialize polymerization. The reaction was carried out at 26 °C for 80 min.

The size and size distribution of the resultant PAA microgels at pH = 3.2 and pH = 7.4, characterized by dynamic light scattering measurement, are given in Figure 7. The average hydrodynamic radius $\langle R_h \rangle$ at pH = 3.2 is smaller than at pH = 7.4. Decreasing particle size is caused by strong hydrogen bonding of the PAA at pH = 3.2. As the microgels were at pH = 3.2, the loose surface chains may collapse, resulting in a narrower particle size distribution. In both cases, the single particle size distribution peak showed that the HPC macromolecular chains were inside the PAA microgels.

Conclusion

The phase transition behavior of hydroxypropylcellulose (HPC) and poly(acrylic acid) (PAA) complex system in water has been investigated. The LCST of the complex shifted to much lower temperature than that of the pure HPC as a complexation agent at pH = 3.2. The decrease of the phase transition temperature is attributed to strong hydrogen bonding between the HPC and PAA. The LCST of the complexes decreased with the increase of the molecular weight of either HPC or PAA. As the pH value increases from 4.0 to 7.4, the LCST of the HPC−PAA complex decreases. This may be due to the salt effect of the polyelectrolyte on the nonionic polymer. The dilute HPC/PAA aqueous solution at pH = 3.2 can form interpolymer complexation near room temperature, and the associated nanoparticle sizes decreased with increasing temperature. The complexation between HPC and PAA leads to a new method for the formation of surfactant-free microgels at room temperature. The resultant microgels swell and collapse at the pH value higher and lower than the pK_α value of the PAA, respectively.

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