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Steric Stabilization of Thermally Responsive N-isopropylacrylamide Particles by Poly(vinyl alcohol)

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Abstract

Poly(vinyl alcohol) (PVA) was used as a steric stabilizer for the dispersion polymerization of crosslinked poly(*N*-isopropylacrylamide) (PNIPAM) in water. A series of reactions were carried out using PVA of varying molecular weight and degree of hydrolysis. Under appropriate conditions, PNIPAM particles of uniform and controllable size were produced using PVA as the stabilizer. The colloidal stability was investigated by measuring changes in particle size with temperature in aqueous suspensions of varying ionic strength. For comparison, parallel colloidal stability measurements were conducted on PNIPAM particles synthesized with low molecular weight ionic surfactants. The PVA provides colloidal stability over a wide range of temperature and ionic strength, whereas particles produced with ionic surfactants flocculate in moderate ionic strength solutions upon collapse of the hydrogel as temperature is increased. Experimental results and theoretical consideration indicate sterically stabilized PNIPAM particles resulted from grafting of PVA to the PNIPAM particle surface. The enhanced colloidal stability afforded by PVA allows the temperature responsive PNIPAM particles to be used under physiological conditions where electrostatic stability is ineffective.

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known water soluble polymer that is often crosslinked to form temperature sensitive hydrogels. The crosslinked PNIPAM polymer network is swollen by water near room temperature and collapses upon heating above the volume phase transition temperature (VPTT) of ~33°C.¹ Below the VPTT, favorable NIPAM-water interactions cause the hydrogel to expand. Above the VPTT, water is expelled from the hydrogel due to an entropically driven phase separation, resulting in a significant decrease in the hydrogel volume.² A variety of functional monomers may be copolymerized with PNIPAM to obtain hydrogels that respond to changes in pH,^{3–4} ionic strength,⁴ light,⁵ and electric fields^{6–8} as well as temperature. The ability to induce macroscopic physical changes with minute environmental stimuli enables PNIPAM-based hydrogels to be used in a variety of applications, including on-off switches,⁹ valves,¹⁰ optical devices,^{11–12} intelligent sensors,¹³ membranes,¹⁴ chemo-mechanical devices,¹⁵ and controlled drug delivery.¹⁶

Many of the potential applications of PNIPAM-based hydrogels require that they are in the form of stable colloidal dispersions with uniform size distribution, or “microgels”.^{17–18} The size of microgel particles can be adjusted by changing temperature, pH, ionic strength, or other factors that influence the degree of swelling of the particles by water. PNIPAM microgels are commonly synthesized via dispersion polymerization in water to give electrostatically charged particles. The electrostatic charge on PNIPAM microgels is

imparted during synthesis either through ionic free radical initiators,¹⁹ or through ionic surfactants added to enhance colloidal stability and control particle size.^{20–21} In the expanded state below the VPTT, the particles are prevented from aggregating through a combination of steric effects from dangling PNIPAM chains and electrostatic repulsion between particles. Electrostatic repulsion is solely responsible for preventing particles from aggregating above the VPTT, where the PNIPAM chains are in the collapsed state. As a result, PNIPAM microgel particles aggregate above the VPTT in suspensions of moderate to high ionic strength due to the loss of electrostatic repulsion and the increase in effective Hamaker constant as water is expelled from the particles.²² The aggregation of PNIPAM particles is a particular problem for biomedical applications, because colloidal stability is not maintained in typical buffer solutions at or near physiological temperature.

To overcome these limitations, the present study investigates enhancement of colloidal stability of PNIPAM particle via steric stabilization. Steric stabilization has the significant advantage over electrostatic stabilization in that it is typically insensitive to electrolyte concentration of the solvent. An effective steric stabilizer is compatible with the surrounding solvent, and extends out far enough to create a repulsive barrier to prevent aggregation.²³ The stability of PNIPAM microgel particles could be significantly enhanced by the addition of a stabilizing layer that does not collapse at the VPTT. In this way, PNIPAM particles can be synthesized that are colloidally stable over a wide range of ionic strength both above and below the VPTT. Despite the advantages of steric stabilization, there have been few reports on the synthesis of sterically stabilized microgel particles, and little focus on the enhancement of colloidal stability.^{24–25}

In the present study, poly(vinyl alcohol) (PVA) was investigated as a steric stabilizer for PNIPAM microgels. PVA is a water soluble, nontoxic, biodegradable polymer that is widely used as an emulsifier for oils and polymers.^{26–28} PVA has been used successfully as a steric stabilizer in the dispersion polymerization of aniline, methyl methacrylate, styrene, and acrylic acid.^{29–32} Since PVA is synthesized by the hydrolysis of poly(vinyl acetate), it is commercially available as random copolymers of vinyl alcohol and vinyl acetate. The residual vinyl acetate groups from partial hydrolysis give the PVA amphiphilic character, as the vinyl acetate groups interact favorably with oils and the vinyl alcohol groups interact favorably with water.³³ In addition to physical adsorption, PVA can become covalently grafted to the surface of polymer particles during dispersion polymerization.³¹ It is expected that microgel particles with adsorbed or grafted PVA will display significantly enhanced colloidal stability compared to electrostatically stabilized particles. The improved stability would allow the particles to be used under wide ranges of temperature, pH, and ionic strength, including physiological conditions where microgels typically coagulate.

2. Materials and Methods

2.1 Materials

N-isopropylacrylamide (NIPAM), N,N'-methylene(bis)acrylamide (BIS), sodium dodecyl sulfate (SDS), trimethyltetradecylammonium bromide (TTAB), potassium persulfate (KPS) and poly(vinyl alcohol) (PVA) were purchased from Sigma Aldrich and used as received. Four types of PVA were investigated, two different molecular weights, each with two different degrees of hydrolysis: 31,000–50,000 g/mol (88–89% and 98–99% vinyl alcohol) and 146,000–186,000 g/mol (88–89% and 98–99% vinyl alcohol). The initiator 2, 2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (AIBI) or VA-044 was purchased from Wako Chemical and used as received.

2.2 Synthesis and Characterization of PNIPAM Particles

Dispersion polymerization was carried out in a 250 mL round bottom flask filled with 40 mL of de-ionized water, 0.38 g NIPAM monomer, 0.34 g BIS cross-linker and PVA stabilizer. The solutions were heated to 90°C under an argon atmosphere with continuous stirring for 1.5 hours to fully dissolve the PVA. The temperature was then lowered to 60°C for 30 min prior to injecting 0.1 g AIBI initiator dissolved in 2.5 mL deionized water. The polymerization was carried out for 5 hours at 60°C with continuous stirring

For comparison, cationic (+PANIPAM) and anionic (–PINIPAM) particles were synthesized using methods reported in the literature. For anionic PNIPAM, 1.47 g NIPAM monomer, 0.012 g SDS surfactant, and 0.147 g BIS cross-linker were added to 95 mL deionized water in a 250 mL round bottom flask. For cationic PNIPAM, 1.05 g NIPAM monomer, 0.6 g TTAB surfactant, and 0.035 g BIS cross-linker were added to 95 mL deionized water in a 250 mL round bottom flask. The solutions were heated to 60°C under an argon atmosphere while continuously stirring for 40 min. To start the reaction, the initiator was dissolved in 5 mL of deionized water and added via syringe. For anionic PNIPAM, 0.059 g of the anionic initiator KPS were used. For cationic PNIPAM, 0.075 g of the cationic initiator AIBI were used. The polymerization was carried out at 60°C for 5 hours in both cases.

At the completion of polymerization, particles were washed four times by centrifugation and re-dispersing in pure deionized water. Yields were determined gravimetrically. A Brookhaven Instruments model 90 Plus particle size analyzer was used to characterize the average particle diameter as a function of temperature. Ionic strength was adjusted by addition of KCl to the microgel suspensions.

In light scattering measurements, the viscosity of the continuous phase is needed to obtain the hydrodynamic diameter from the Stokes-Einstein equation. The viscosity of pure water at the measurement temperature was used for all KCl solutions, since KCl has a minor affect on viscosity at the concentrations used. For light scattering measurements in PVA solutions, the measured viscosity was used. The viscosities of PVA solutions were measured from 25–40°C using a Cannon-Fenske routine viscometer (Cannon Instrument Co., State College, PA) in a constant temperature water bath.

3. Results and Discussion

To determine the most favorable conditions for dispersion polymerization of NIPAM using PVA as the stabilizer, a matrix of experiments was completed, as shown in Table 1. The reactions were carried out with a range of PVA concentrations grouped as low (6–21 wt% PVA/NIPAM) and high (300–700 wt% PVA/NIPAM). For each experiment, the effectiveness of the stabilizer was characterized by its ability to maintain colloidal stability during the reaction, to produce particles of narrow size distribution, and to stabilize particles in 100 mM KCl after washing off excess PVA. Partially hydrolyzed PVA was most effective at stabilizing particles during the reaction at low concentrations, while fully hydrolyzed PVA was most effective at high concentrations. Only particles produced with high concentrations of low molecular weight, fully hydrolyzed PVA remained stable in 100 mM KCl after washing off excess PVA.

In dispersion polymerization, the initial particle formation is through homogeneous nucleation. The nucleated particles coagulate to lower interfacial free energy until the amount of adsorbed or grafted stabilizer is high enough to provide sufficient colloidal stabilization.³⁴ In the case of PVA, stabilization can be achieved by adsorption onto the particle surface, chemical grafting to the particles via hydrogen abstraction, or a

combination of the two effects. The number of particles becomes fixed after they are stabilized. The particles continue to grow by absorption of oligomeric radicals from the surrounding solution and polymerization within the particle phase.³⁴ The stabilizer therefore controls the number of particles formed, and thus the final particle size.

Increasing the stabilizer concentration causes the particle size to decrease, as the stabilizer is able to cover a larger total interfacial area. If the stabilizer were completely adsorbed on the particle surface, the total interfacial area would be proportional to the number of stabilizer molecules and a log-log plot of particle diameter versus stabilizer concentration would have a slope of -1.35. Figure 1 shows a log-log plot of PNIPAM particle diameter at 25°C versus PVA concentration. The resulting exponential relationship between particle diameter (D) and stabilizer concentration is $D \sim [\text{PVA}]^{-0.57}$ and $D \sim [\text{PVA}]^{-0.37}$ for partially hydrolyzed and fully hydrolyzed low molecular weight PVA respectively. In comparison, a similar study of PNIPAM dispersion polymerization with SDS yielded $D \sim [\text{SDS}]^{-0.71}$.³⁶ Therefore, neither type of PVA is as surface active as SDS. It is interesting to note that partially hydrolyzed PVA is more surface active than fully hydrolyzed PVA even though it is less effective at stabilizing the dispersion polymerization. The residual hydrophobic vinyl acetate groups give the partially hydrolyzed PVA more amphiphilic character. In non-reacting suspensions, it has been shown that partially hydrolyzed PVA provides colloidal stability while fully hydrolyzed PVA does not because it is less surface-active.^{26, 37} The results suggest that the fully hydrolyzed PVA is effective as a stabilizer in PNIPAM synthesis due to chemical grafting rather than strong adsorption onto the particles.

Figure 2 shows average PNIPAM particle diameter in deionized water versus temperature for samples produced with the four types of PVA using a fixed concentration of 11 wt% PVA/NIPAM. The particles display the expected temperature dependent change in diameter, with the collapse of the hydrogel structure with increasing temperature. The VPTT of the samples was determined by the inflection point of the Boltzmann sigmoid equation fit of the data, and was approximately 32°C for all four samples in the figure. Comparing the two curves with partially hydrolyzed PVA shows that increasing PVA molecular weight results in a slight decrease in overall particle size, as the longer partially hydrolyzed PVA chains are able to stabilize a larger surface area upon adsorption. However, increasing the molecular weight of fully hydrolyzed PVA results in a significant increase in overall particle size. The PVA molecular weight effect on particle size shown in Figure 2 is further evidence that stabilization by fully hydrolyzed PVA is through chemical grafting rather than adsorption. Previous studies of emulsion and dispersion polymerization have shown that PVA can become grafted to particle surfaces through hydrogen abstraction reactions with free radicals.^{31, 38} Therefore, it is likely that PNIPAM chains graft to PVA during the course of the reaction. The graft copolymers that form *in situ* with higher molecular weight PVA will be more water soluble and less likely to stabilize the PNIPAM until later in the reaction, resulting in larger particle size.

As shown in Table 1, PNIPAM particles synthesized with high concentrations of low molecular weight, fully hydrolyzed PVA remained stable in 100 mM KCl after washing off excess PVA. The observed colloidal stability in 100 mM KCl after washing the particles indicates that enough fully hydrolyzed PVA is chemically grafted to PNIPAM to provide steric stabilization, while partially hydrolyzed PVA is weakly adsorbed and largely removed by washing. Colloidal stability in electrolyte solutions was examined in more detail using a series of PNIPAM samples produced with varying concentrations of fully hydrolyzed low molecular weight PVA. These samples were produced with PVA/NIPAM reactant ratios of 3.3, 4.0, 5.0 and 6.7 and were named 3.3PVA-PNIPAM, 4.0PVA-PNIPAM, 5.0PVA-PNIPAM, and 6.7PVA-PNIPAM, respectively. Table 2 lists the yield, swelling ratio, and polydispersity index (PDI) for each of these samples. The PDI shown was recorded at 25°C

using the method of cummulants analysis with light scattering data. Using this analysis, a monodisperse sized sample would have a PDI of 0. The PDI data indicates that the particles have a near monodisperse size distribution that does not change significantly with temperature for any of the samples in deionized water. The polydispersity was similar to that of cationic (+PNIPAM) and anionic (−PNIPAM) particles produced using methods previously reported in the literature (shown on Table 2). The swelling ratio, defined as the cube of the average diameter at 25°C divided by the cube of the average diameter at 40°C, did not depend on the PVA/NIPAM reactant ratio. The incorporation of hydrophilic moieties is known to favor a more gradual volume transition, and a decrease in the swelling ratio.³⁹ Since the measured swelling ratio did not change systematically with PVA concentration, it can be inferred that the amount of PVA incorporated in the hydrogel interior does not change significantly in the four samples. It is also possible that PVA incorporation is largely confined to the particle surface. All of the PVA stabilized samples were produced with the same BIS:NIPAM reactant ratio and are therefore expected to have similar crosslink densities. The +PNIPAM sample was synthesized with a much lower BIS:NIPAM ratio, and thus has a lower crosslink density and a much higher swelling ratio. All of the PVA-stabilized samples shown in Table 2 were stable in 100 mM KCl, whereas the +PNIPAM and −PNIPAM samples flocculated above 33°C

Figure 3 shows the average particle diameter in deionized water versus temperature from 25–40°C for the six samples in Table 2. As expected, the particle size decreases as the temperature is increased. The VPTT was defined as the temperature where the fitted Boltzmann sigmoid equation has an inflection point. The VPTT of both +PNIPAM and −PNIPAM latexes was 33°C. The PVA stabilized latexes, on the other hand, had higher VPTT of 34–36°C. The VPTT of the PVA stabilized latexes did not change systematically with PVA/NIPAM reactant ratio used in the synthesis. Similar increases in VPTT have been reported for PNIPAM microgel particles modified by the grafting of hydrophilic monomer that opposes the collapse of the hydrogel.³⁹ The shift in VPTT indicates that some fraction of the PVA is incorporated into the hydrogel interior. However, since all four PVA samples have similar swelling ratios, the amount of PVA incorporated into the interior does not appear to change significantly within the range of PVA/PNIPAM reactant ratios investigated.

The series of latexes synthesized with PVA display significantly improved colloidal stability in electrolyte solutions compared to the electrostatically stabilized −PNIPAM and +PNIPAM latexes. In Figures 4 and 5, the average diameter measured by dynamic light scattering is plotted versus temperature for microgel particles suspended in 0.01 M and 0.1 M KCl. The electrostatically stabilized latexes are observed to flocculate above the VPTT in both 0.01 M and 0.1 M KCl. Flocculation is noted by a large increase in diameter and PDI measured by dynamic light scattering. Measurements were stopped immediately after particle flocculation for the ionically stabilized latexes. In contrast, the PVA stabilized latexes are stable above the VPTT and display the expected decrease in diameter above the VPTT due to the temperature-induced collapse of the microgels. Also, no significant change in the PDI occurs with temperature for the PVA stabilized samples, indicating no measurable aggregation. The results indicate that the PVA sterically stabilizes the particles so that colloidal stability is insensitive to ionic strength both above and below the VPTT.

To explore if simple adsorption of PVA was sufficient to stabilize PNIPAM, a latex that lacked steric stability (+PNIPAM) was exposed to fully hydrolyzed PVA for the same time, temperature, and PVA concentration used in the polymerization reaction. An aliquot of the latex +PNIPAM was placed into an aqueous solution of fully hydrolyzed PVA at a concentration of 3% (w/v). This was heated to 90°C, stirred at 500 rpm for 1.5 hrs, then cooled to 60°C for 30 min. The solution was then stirred for an additional 5 hrs at 60°C to

simulate the conditions used to synthesize the 3.3PVA-PNIPAM sample. The sample was then cleaned by washing the particles four times with deionized water. As seen in Figure 6, the resulting particles are stable in deionized water, but flocculate at 34°C and 32°C in 0.01M KCl and 0.1M KCl respectively. It is apparent that little or no PVA remained attached to the surface of the +PNIPAM particles after washing. The flocculation temperature also clearly decreases with increasing ionic strength, as is consistent with previous studies of electrostatically stabilized PNIPAM microgels.²²

Additional investigation of PVA adsorption onto +PNIPAM was carried out by measuring the temperature dependence of particle diameter in aqueous solutions of 1% (w/v) PVA. The measurements were done using both the fully and partially hydrolyzed PVA in solutions of 0.01 M KCl and 0.1 M KCl, as shown in Figure 7. The latex flocculated above ~31°C in 0.1 M KCl and ~33°C in 0.01 M KCl with both fully hydrolyzed and partially hydrolyzed PVA. However, repeated size measurements above the flocculation temperature (not shown) show a more gradual increase in diameter over time with partially hydrolyzed PVA, indicating slower flocculation kinetics. Differences in flocculation kinetics may be due to the greater surface activity of the partially hydrolyzed PVA, which can lead to a greater extent of surface coverage. It is possible that as the particles collapse, enhanced hydrophobicity of the PNIPAM microgel surface strengthens its interaction with hydrophobic acetate groups. Regardless, physically adsorbed PVA alone can only slow the PNIPAM coagulation above the VPTT and not prevent it. In addition, increasing the PVA concentration in solution did not enhance colloidal stability. The observed flocculation temperature in 0.01 M KCl was reduced to ~27°C when the PVA concentration was increased to 3% (w/v). Excess PVA in aqueous solution has been shown to destabilize particles via a depletion flocculation mechanism.⁴⁰ These results show that increasing the PVA concentration in the surrounding solution does not result in stabilization by physically adsorbed polymer, but rather destabilizes the particles.

Conclusions

PVA is an effective steric stabilizer for the aqueous dispersion polymerization of NIPAM. Monodisperse sized PNIPAM particles can be formed that are colloiddally stable over a much wider range of ionic strength than is possible with ionic surfactant stabilizers. Although partially hydrolyzed PVA is more surface active than fully hydrolyzed PVA, the fully hydrolyzed version is a more effective steric stabilizer in dispersion polymerization due to chemical grafting of the PVA to the surface of the PNIPAM particles. Studies of PNIPAM particles with adsorbed PVA demonstrate that physical adsorption is insufficient to stabilize particles above the VPTT. The PNIPAM particles with PVA grafted to the surface, on the other hand, are stable at temperatures both above and below the VPTT in relatively concentrated electrolyte solution. In all cases, PNIPAM particles synthesized with ionic surfactant stabilizers coagulate above the VPTT due to screening of electrostatic repulsion by the surrounding electrolyte solution. The enhanced colloidal stability obtained with grafted PVA enables PNIPAM particles to be used under a wider range of temperature, pH, and ionic strength, including physiological conditions where electrostatically stabilized PNIPAM coagulates. The PVA stabilized particles thus have promise in drug delivery and other biological applications.

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Bibliography

1. Wu C. *Polymer*. 1998; 39:4609–4619.
2. Otake K, Inomata H, Konno M, Saito S. *Macromolecules*. 1990; 23:283–289.
3. Annaka M, Tanaka T. *Nature*. 1992; 355:430–432.
4. Snowden JM, Chowdhry BZ, Vincent B, Morris GE. *J. Chem., Faraday Trans.* 1996; 92:5013–5016.
5. Suzuki A, Tanaka T. *Nature*. 1990; 346:345–347.
6. Kwon C, Bae YH, Kim SW. *Nature*. 1991; 354:291–293. [PubMed: 1956379]
7. Lowe TL, Virtanen J, Tenhu H. *Langmuir*. 1999; 15:4259–4265.
8. Tanaka T, Nishio I, Sun S-T, Ueno-Nishio S. *Science*. 1982; 218:467–469. [PubMed: 17808541]
9. Bae YH, O Teruo, Hsu Richard, Kim SW. *Makromol. chem., Rapid Commun.* 1987; 8:481–485.
10. Okahata Y, Noguchi H, Seki T. *Macromolecules*. 1986; 19:493–494.
11. Tsutsui H, Akashi R. *Journal of Applied Polymer Science*. 2006; 102:362–368.
12. Reese CE, Mikhonin AV, Kamenjicki M, Tikhonov A, Asher SA. *J. Am. Chem. Soc.* 2004; 126:1493–1496. [PubMed: 14759207]
13. Asher SA, Peteu SF, Reese CE, Lin MX, Finegold D. *Anal. Bioanal. Chem.* 2002; 373:632–638. [PubMed: 12185576]
14. Ito T, Hioki T, Yamaguchi T, Shinbo T, Nakau S, Kimura S. *J. Am. Chem. Soc.* 2002; 124:7840–7846. [PubMed: 12083938]
15. Brazel CS, Peppas NA. *Macromolecules*. 1995; 28:8016–8020.
16. Qiu Y, Park K. *Adv. Drug Delivery Rev.* 2001; 53:321–339.
17. Elaissari A. *Progr Colloid Polym Sci.* 2006; 133:9–14.
18. Saunders BR, Vincent B. *Adv. Coll. Int. Sci.* 1999; 80:1–25.
19. Pelton RH, Chibante P. *Colloids Surf.* 1986; 20:247–256.
20. McPhee W, Tam KC, Pelton R. *J. Coll. Int. Sci.* 1993; 156:24–30.
21. Tam KC, Ragaram S, Pelton RH. *Langmuir*. 1994; 10:418–422.
22. Rasmusson M, Routh A, Vincent B. *Langmuir*. 2004; 20:3536–3542. [PubMed: 15875381]
23. Napper, DH. *Polymeric Stabilization of Colloidal Dispersions*. New York: Academic Press; 1984.
24. Dupin D, Fujii S, Armes P, Reeve P, Baxter SM. *Langmuir*. 2006; 22:3381–3387. [PubMed: 16548605]
25. Yin J, Dupin D, Li J, Armes SP, Liu S. *Langmuir*. 2008; 24:9334–9340. [PubMed: 18642939]
26. Finch, CA. *Polyvinyl Alcohol: Properties and Applications*. New York: John Wiley & Sons; 1973.
27. Okaya T, Suzuki A, Kikuchi K. *Colloids Surf.* 1999; 153:123–125.
28. Yuki K, Nakameae M, Sato T, Murayama H, Okaya T. *Polymer International*. 2000; 49:1629–1635.
29. Stejskal J, Kratochvil P, Helmstedt M. *Langmuir*. 1996; 12:3389–3392.
30. Kim OK, Lee K, Kim K, Lee BH, Choe S. *Colloid. Polym. Sci.* 2006; 284:909–915.
31. Hong J, Hong CK, Shim SE. *Colloids Surf., A.* 2007; 302:225–233.
32. Minami H, Kimura A, Kinoshita K, Okubo M. *Langmuir*. 2010; 26:6303–6307. [PubMed: 20043688]
33. Gilmore CM, Poehlein GW, Schork FJ. *J. Appl. Polym. Sci.* 1993; 48:1449–1460.
34. Kawaguchi, S.; Ito, K. *Advances in Polymer Science*. Okubo, M., editor. Vol. Vol. 175. Berlin, Germany: Springer; 2005. p. 299
35. Paine AJ, L W, McNulty J. *Macromolecules*. 1990; 23:3104–3109.
36. Wu X, Pelton RH, Hamielec AE, Woods DR, McPhee W. *Colloid and Polymer Science*. 1994; 272:467–477.
37. Noro K. *Br. Polym. J.* 1970; 2:128–134.
38. Kim N, Sudol ED, Dimonie VL, El-Aasser MS. *Macromolecules*. 2004; 37:3180–3187.
39. Gan D, Lyon LA. *Macromolecules*. 2002; 35:9634–9639.
40. Khan AU, Briscoe BJ, Luckham PF. *Colloids Surf., A.* 2000; 161:243–257.

Figure 1.

Linear fit to the logarithm of PNIPAM particle diameter (nm) versus logarithm of PVA concentration (g/L) for fully hydrolyzed (slope of -0.37) and partially hydrolyzed (slope of -0.57) PVA (MW = 31,000–50,000 g/mol). The linear regression gives an R^2 value of 0.98 in both cases.

Figure 2. Particle diameter in deionized water versus temperature for PNIPAM synthesized with 11 wt % PVA/NIPAM. The curves are Boltzmann sigmoid equation fits of the data.

Figure 3. Temperature dependence of PNIPAM particle size in deionized water. The curves are Boltzmann sigmoid equation fits of the data.

Figure 4. Temperature dependence of PNIPAM particle size in 0.01 M KCl. The solid curves are Boltzmann sigmoid equation fits of the data. The dotted curves show the increase in diameter due to flocculation of the electrostatically stabilized particles.

Figure 5. Temperature dependence of PNIPAM particle size in 0.1 M KCl. The solid curves are Boltzmann sigmoid equation fits of the data. The dotted curves show the increase in diameter due to flocculation of the electrostatically stabilized particles.

Figure 6.

Cationic PNIPAM (+PNIPAM) after exposure to PVA at temperatures, times, and PVA concentrations that replicate the synthesis of 3.3PVA-PNIPAM. Excess PVA was removed prior to measuring size. Solid curves are Boltzmann sigmoid equation fits to data. Dotted lines indicate the increase in diameter due to flocculation.

Figure 7.

Particle size versus temperature for +PNIPAM dispersed in 1% (w/v) PVA (MW = 31000–50000 g/mol). Square symbols and dashed lines are data in 0.1M KCl. Circles and solid lines are data in 0.01M KCl.

Summary of matrix of polymerization experiments to determine the effectiveness of PVA as a steric stabilizer in dispersion polymerization of NIPAM.

Table 1

PVA Molecular Weight	PVA Degree of Hydrolysis	PVA/NIPAM Reactant Ratio	Stable during reaction?	Low PDI?	Stable in 0.1M KCl after cleaning?
31k-50k	88%-89%	300%-700%	No	No	No
31k-50k	98%-99%	300%-700%	Yes	Yes	Yes
146k-186k	88%-89%	300%-700%	No	No	No
146k-186k	98%-99%	300%-700%	Yes	No	No
31k-50k	88%-89%	6%-21%	Yes	Yes	No
31k-50k	98%-99%	6%-21%	Yes	No	No
146k-186k	88%-89%	6%-21%	Yes	Yes	No
146k-186k	98%-99%	6%-21%	Yes	No	No

Table 2

Properties of microgels synthesized with fully hydrolyzed PVA compared to typical electrostatically stabilized PNIPAM. Polydispersity index (PDI) is calculated by the method of cumulants using DLS. Swelling ratios (SR) calculated by $(\text{Diameter at } 25^{\circ}\text{C})^3/(\text{Diameter at } 40^{\circ}\text{C})^3$. Yields were calculated as $((\text{mass of obtained polymer})/(\text{mass of initial monomers}))*100$.

Microgel Sample	Flocculation Temperature in 0.1 M KCl	PDI	Swelling Ratio	Yield (%)
3.3PVA-PNIPAM	Stable	0.07	5.3	65
4.0PVA-PNIPAM	Stable	0.07	5.5	69
5.0PVA-PNIPAM	Stable	0.06	5.1	75
6.7PVA-PNIPAM	Stable	0.06	5.2	82
-PNIPAM	33°C	0.08	4.5	89
+PNIPAM	33°C	0.06	14.4	76