Synthesis and Solution Properties of Poly(*N*-isopropylacrylamide-*co*-diallyldimethylammonium chloride)

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ABSTRACT: A series of copolymers of *N*-isopropylacrylamide (NIPAM) and diallyldimethylammonium chloride (DADMAC) were synthesized and characterized. Copolymer molecular weight decreased with increasing DADMAC content. The copolymers were soluble in water at temperatures below the cloud point temperature (CPT) and formed stable colloidal particles above the CPT. The CPT of the copolymer decreased as the salt concentration increased. The size and stability of the colloidal particles were NaCl concentration dependent. At salt concentrations higher than 0.1 M, coagulation was observed. At lower ionic strengths the particles were colloidally stable and the average diameters increased with salt concentration. Particle sizes were also pH dependent, and it was concluded that pH sensitivity was simply an ionic strength effect.

Introduction

Poly(*N*-isopropylacrylamide) (polyNIPAM) is a linear nonionic polymer which is water soluble at low temperature but phase separates when the temperature is raised above the cloud point temperature (CPT) of 32 °C. The unusual solubility behavior of polyNIPAM in water has resulted in applications in biotechnology, drug release, instant film technology, flocculation, and water treatment.[1–4]

PolyNIPAM derivatives and copolymers can also show temperature sensitivity.[5–9] For example, Chiklis et al.[7] observed that the CPT of a 5% polyNIPAM solution increased with the acrylamide (AM) content in copolymers and disappeared when the AM content increased beyond 34 mol %. For ionic copolymers of NIPAM, Guillet et al.[3] reported that both anionic and cationic segments in the polymer chains could increase the CPT of the polymer solution.

Poly(diallyldimethylammonium chloride) (polyDADMAC) and poly(acrylamide-*co*-diallyldimethylammonium chloride) are positively charged polymers which are widely used as flocculants. On the other hand, the patent of Guillet et al.[3] is the only reference to the use of cationic polyNIPAM copolymers as flocculants. The potential advantages of polyNIPAM-based flocculants are that flocculation may be temperature sensitive and that the *N*-isopropyl group may protect the amide from hydrolysis in extremely caustic environments.

The objectives of this work were to synthesize and characterize a series of NIPAM/DADMAC copolymers. It is an interesting property of these materials that above the CPT the phase-separated polymer is present as a stable colloidal dispersion. In these conditions the behavior of the phase-separated copolymer particles is similar to that of cross-linked polyNIPAM microgel particles first reported by Pelton and Chibante.[10] Below the CPT of polyNIPAM (32 °C) the microgels contain about 90% water whereas above the CPT the water content drops to about 20%, corresponding to 2 water molecules per amide group.[11,12]

Reported in this work are the preparation and properties of polyNIPAM/DADMAC copolymers as functions of temperature and ionic strength. This work forms the foundation for future studies of the temperature dependence of colloidal flocculation with the copolymers.

Experimental Section

(a) Materials. NIPAM (Kodak) was purified by dissolution in toluene and recrystallization with *n*-hexane. DADMAC (Aldrich, 60% aqueous solution) was precipitated by the addition of acetone and dried under vacuum at room temperature. Potassium persulfate (KPS) (BDH, analytical grade) and $FeCl_2 \cdot 4H_2O$ (Fisher Certified) were used as received. The potassium salt of poly(vinyl sulfate) and toluidine blue were kindly supplied by Nalco Chemicals Inc.. All aqueous solutions were made with Milli Q water.

(b) Copolymer Synthesis and Characterization. The copolymerization was carried out in a 250 mL two-neck flask fitted with a nitrogen bubbling tube and a vent. For the preparation of copolymer A-26-8, 0.0353 mol of DADMAC and 0.0925 mol of NIPAM were dissolved in 150 mL of Milli Q water. After the system was purged with nitrogen for 30 min while stirring with a magnetic stirrer, 0.02 g of KPS and 0.02 g of $FeCl_2 \cdot 4H_2O$ in 5 mL of water were injected into the system and the reaction was allowed to proceed for 2 h in an ice-water bath. The copolymer was precipitated by the addition of NaCl at ~40 °C (×3). The precipitated copolymer was dissolved in water and dialyzed against water using a Spectrapor tubing with a molecular weight cutoff of 12 000 to give a final dialysate conductivity of less than 1 μS/cm. The final product was dried at room temperature.

Copolymer compositions were obtained by colloidal titration using 0.001 M potassium poly(vinyl sulfate) (PVSK) solution as the titrant and toluidine blue as as indicator.[13,14] The PVSK solution was standardized with polyDADMAC solution. The copolymer of NIPAM/DADMAC of known weight (0.3–0.5 g) was dissolved in 30 mL of Milli Q water, and two drops of 0.1% toluidine blue were added. A distinct color change from blue to reddish-purple during the titration indicated the end point.

The molecular weights of the copolymers were obtained through the use of a Chromatix KMX-6 low-angle light scattering photometer with a cell length of 15 mm and a field stop of 0.2. This corresponded to an average scattering angle of 4.8°. The refractive index increments of the copolymer aqueous solutions were determined using a Chromatix KMX-16 laser differential refractometer at 25 °C and a wavelength of 632.8 nm. The solvent (Milli Q water) and solutions of the copolymer in Milli Q water were clarified by filtration through 0.22 and 0.45 μm filters (Millipore), respectively.

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Table 1. Polymer Preparation Conditions and Compositions

				fraction in feed[a] (mol %)		fraction in polymer (mol %)		
sample	temp (°C)	KPS (g)	$FeCl_2$ (g)	DADMAC	NIPAM	DADMAC	NIPAM	$M_w/10^5$ (g/mol)
A-28-10	0	0.036	0.034	12.8	87.2	0.87	99.13	1.1
A-18-6	23	0.041	0	20.7	79.1	1.09	98.91	1.6
A-26-8	0	0.022	0.020	27.6	72.4	2.19	97.81	2.4

[a] Based on the total monomers.

The difficulties in characterizing polyelectrolytes by light scattering are documented in the literature.[15-17] However, the copolymers prepared in this work had a low charge content (0.87–2.19 mol % DADMAC; see Table 1) so no special precautions were taken. The uncertainty of the molecular weight determined by light scattering was estimated at ±10%.

(c) Colloidal Properties of the Copolymers. The phase separation temperatures of the copolymers were measured using static light scattering or UV (transmittance). Static light scattering measurements were made using a Sofica PGD 40B photogoniometer with an incident wavelength of 546 nm and detection at a scattering angle of 90°. Light scattering intensities, relative to that from a glass standard, were measured as the temperature was raised at a rate of 1–2 °C min^{-1}.

The transmittance of ~1 wt % copolymer solutions at different pH values and salt concentrations was measured using an HP 8452 diode array UV/vis spectrophotometer (Hewlett-Packard) at a wavelength of 500 nm as temperature increased from 23 to 55 °C. Water was used as the blank.

The average diameters of the colloidal particles which formed from the aggregated copolymer chains above the phase separation temperatures were measured with the NICOMP 370 dynamic light scattering (DLS) apparatus at 90°, and data analysis was done with version 3.70 of the NICOMP software. The intensity weighted average diameters are reported in this work.

Electrophoretic mobilities of the colloidal copolymer particles were measured with a Coulter DELSA. The procedures were described in detail elsewhere.[18]

Results

(a) Copolymer Synthesis and Characterization. The preparation conditions and molecular properties of the copolymers are given in Table 1. The molecular weights ranged from 100 000 to 240 000, and the corresponding mole fractions of cationic groups went from 0.9 to 2%. Attempts to extend the series to give higher DADMAC contents were unsuccessful because the polymer molecular weights were below the 12 000 limit of the dialysis tubing and thus were considered not useful as flocculants.

The content of DADMAC in the purified copolymers was less than 1/10 the amount of cationic monomer added to the polymerization. The remaining DADMAC either did not polymerize or formed low molecular weight oligomers which were removed by dialysis. Although direct kinetic data for predicting the copolymerization characteristics of NIPAM/DADMAC are not available from published literature, related studies suggested that the reactivity of DADMAC is much lower than that of NIPAM. Tanaka et al.[19] reported that reactivity ratios were $r_D = 0.58$ and $r_A = 6.7$ for DADMAC and AM, respectively. In an independent study Baade et al.[20] reported the reactivity ratios of $r_D = 0.06$ and $r_A = 6.4$. These results indicated that the reactivity of DADMAC was much lower than that of AM. Furthermore, the reactivity ratios for the AM and NIPAM were found by Priest et al.[8] to equal 1, suggesting NIPAM and AM have identical reactivities toward free radicals in water. Combining these observations, it can be concluded that DADMAC is much less reactive than NIPAM, which is consistent with the results in Table 1.

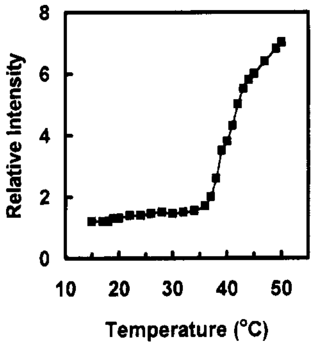

Figure 1. Light scattering intensity vs temperature for 0.01 g/L A-26-10 aqueous solution.

Table 2. Phase Separation Temperatures and Microparticle Sizes of the Copolymer Solutions

	phase separation behavior		particle size		
sample	polym conc (wt %)	CPT (°C)	polym conc (g/L)	temp (°C)	diameter (nm)
A-28-10	1.22	37 ± 0.5	1.2	40	135
A-18-6	1.44	36 ± 0.5	1.2	40	115
A-26-8	1.5	37 ± 0.5	1.2	40	58

(b) Colloidal Properties of the Copolymer Solutions. Aqueous solutions of the copolymer phase separated when the temperature was raised above the cloud point temperature. This is illustrated in Figure 1, which shows the relative scattering intensity of a 10 mg/L solution of copolymer A-26-10 as a function of temperature. There was a sudden increase in light scattering when the temperature passed 36 °C. The colloidal phase was stable. Sols left overnight in the DLS apparatus at elevated temperature showed no indication of sedimentation or aggregation.

The CPTs of more concentrated copolymer solutions measured at pH = 7.4 are given in Table 2. The CPTs of polyNIPAM/DADMAC were about 4 °C higher than that of NIPAM homopolymer (~32 °C); however, the CPT did not change with DADMAC content in the range 0.8–2.2 mol %. Thus, the introduction of up to 2 mol % positively charged groups had little effect on the phase separation behavior of polyNIPAM. This agrees with previous results from our laboratory where it was shown that binding of cationic surfactant (tetradecyltrimethylammonium bromide) to cross-linked polyNIPAM microgel particles caused only a few degrees increase in the phase transition temperature.[21]

The CPT of polyNIPAM homopolymer is remarkably independent of polymer concentration,[1] and we expected the same behavior of our copolymers. The CPTs of A-18-6 at concentrations of 0.42, 0.64, and 1.44% were measured, and no significant differences were observed in this concentration range.

It is interesting to note that above the CPT all three polyNIPAM/DADMAC copolymers formed stable colloidal particles in suspension rather than a macroscopic

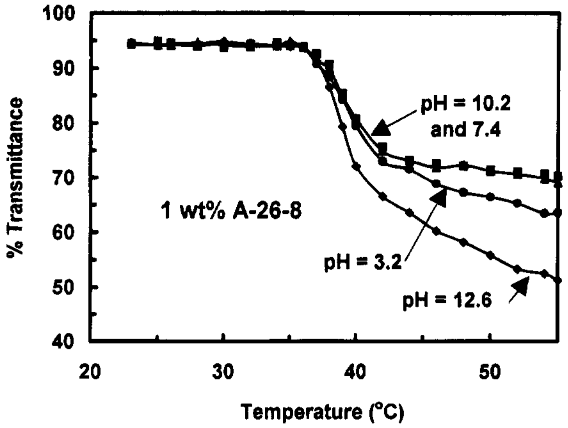

Figure 2. Transmittance of 1 wt % A-26-8 in different pH aqueous solutions against temperature.

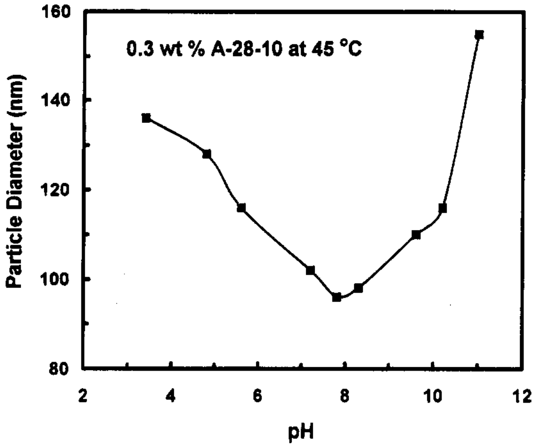

Figure 3. Particle size against pH for 0.3 wt % A-28-10 at 45 °C.

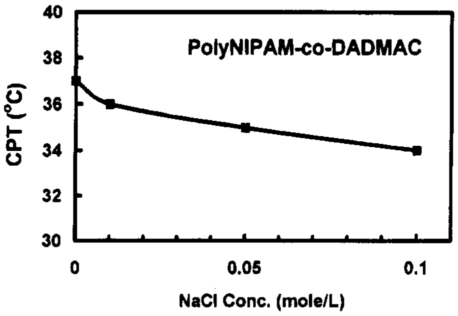

Figure 4. Critical phase separation temperature versus NaCl concentration for 0.3 wt % A-28-10 at pH = 7.2.

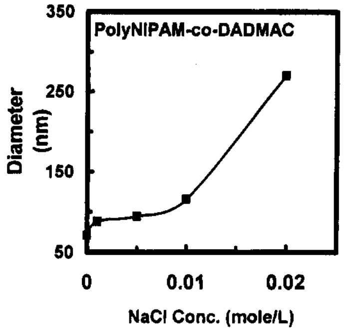

Figure 5. Particle size of 0.2 g/L copolymer A-18-6 vs NaCl concentration at 45 °C.

precipitated phase. The particles formed on heating and disappeared on cooling, and the process was reproducible over a number of cycles in the concentration range of 0.01–25 g/L.

The average diameters of the phase-separated copolymer particles were determined by dynamic light scattering, and the results obtained at 40 °C are given in Table 2. The standard deviations of the particle size distributions were in the range of 20–40% of the mean. The copolymer with the highest DADMAC content gave the smallest particles (58 nm diameter) at 40 °C.

The effect of pH on the CPT of copolymer A-26-A was investigated by transmittance measurements, and the results are shown in Figure 2. The transmittance values for the solutions decreased at the CPT because the phase-separated polymer particles scattered more light than did the homogeneous solution at low temperature; the same effect has been reported for polyNIPAM cross-linked microgel particles.[10] The CPT values, which were taken as the temperatures corresponding to maximum slope in the transmittance/temperature curves, were equal at pH 5.2, 7.4, and 10.2. On the other hand, the CPT values shifted a few degrees to lower temperatures at the extreme pH values of 12.6 and 2.3.

The pH effect on the microparticle stability and particle size was further investigated through light scattering measurements, and the results are shown in Figure 3. It can be seen that the particle size increased as pH changed (both increased and decreased). At extreme pH values no colloidally stable phase was obtained. By contrast, the smallest colloidal stable particles were observed at neutral pH values where the ionic strength was minimum. Since the quaternary ammonium groups are not sensitive to pH, it seems reasonable to interpret the pH effects as mainly ionic strength effects.

The effect of NaCl concentration on the phase separation temperature was determined by transmittance measurements, and the CPT values are shown as a function of electrolyte concentration in Figure 4. It was found that the CPT decreased almost linearly from 37 °C in distilled water to 34 °C in 0.1 M salt. This is consistent with the behavior of polyNIPAM.[22]

The copolymer particle sizes were measured as a function of salt concentration, and results shown in Figure 5 indicated that the higher the salt concentration, the larger the particle size when all other parameters were left unchanged. The standard deviation of the particle size distribution, determined by dynamic light scattering, of the colloidal particles formed by A-18-6 increased with the salt concentration at 45 °C. For a 0.2 g/L A-18-6 solution, the copolymer formed a macroscopic precipitate phase at 45 °C when the NaCl concentration was beyond 0.05 M.

The hydrodynamic diameters of the phase-separated copolymer particles in water and in 0.01 M NaCl solution at different temperatures are given in Figure 6. Increasing temperature from 35 to 40 °C resulted in a rapid decrease in particle size for both solutions. Above 40 °C the particles in water were much smaller than the corresponding particles in 0.01 M NaCl. The particle diameters in salt solution increased from 45 to 55 °C. This behavior contrasts with the behavior of cross-linked polyNIPAM microgel particles whose size is roughly constant above 40 °C.[12] Changes in particle size could reflect both changes in the water content and changes in the number of copolymer chains per particle.

Electrophoretic mobilities of the colloidal copolymer were measured as a function of temperature, and the

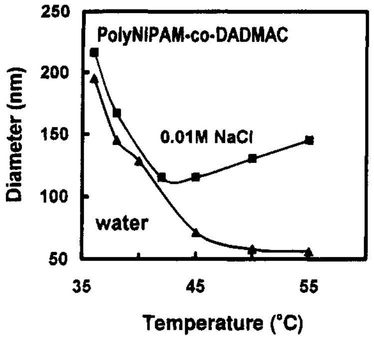

Figure 6. Microparticle size vs temperature for A-18-6 at pH = 7.2.

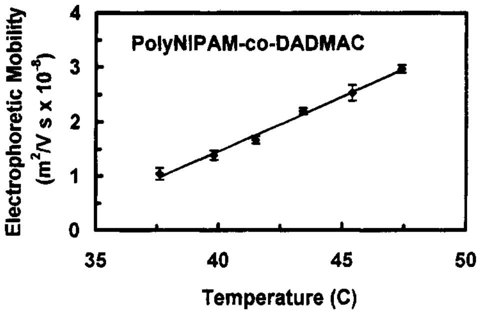

Figure 7. Electrophoretic mobility of phase-separated copolymer A26-8 as a function of temperature. Error bars denote the 90% confidence limits of the Komagata fit of mobility data collected across the cell (see ref 18).

results are summarized in Figure 7. The mobilities increased linearly with temperature, which corresponds to decreasing particle size (see Figure 6). Similar behavior has been reported for cross-linked polyNIPAM microgel particles.[12] The gel particle mobility increases with temperature as the particles expel water because the density of covalently bonded surface charge groups increases.

Discussion

Meewes and co-workers[23] have demonstrated that aqueous polyNIPAM homopolymer undergoes a coil-to-globule transition upon heating where globules are viewed as collapsed, amorphous, polymer chains containing little solvent. The most remarkable feature of our cationic polyNIPAM copolymers was that upon undergoing the coil-to-globule transition at the CPT, the copolymer chains formed stable colloids. The particle diameters varied between 50 and 250 nm depending upon the temperature and ionic strength. Since the colloidal particles formed in the absence of surfactant or other polymers, electrostatic stabilization, originating from the cationic DADMAC groups, would seem the most important stability mechanism. The electrophoresis data (Figure 7) show that mobilities were $\geq 1 \times 10^{-8}$ m²/V, which is usually high enough to confer electrostatic stability.

We believe that very small particles formed when isolated polymer chains underwent coil-to-globule transitions to produce small colloidally unstable particles, which we call precursor particles following the language of the mechanisms for homogeneous nucleation in latex polymerizations.[24,25] The colloidally unstable precursor particles coagulate to produce larger particles. If the positive DADMAC moieties concentrate at the particle–water interface, the surface charge density will increase linearly with particle radius as the particles grow by coagulation because the ratio of surface area to volume will decrease. At the other extreme, if the DADMAC units are uniformly distributed throughout the particles, the surface charge density would be constant. We propose that the narrow colloidal phase particle size distribution observed by DLS indicates that surface charge densities and thus surface potentials are increasing functions of particle diameter. However, it is unlikely that every charge could be located at the particle–water interface. The effects of the two limiting cases, all charges on the surface and constant charge density, on the radius dependence of the stability ratio are illustrated in the following calculation.

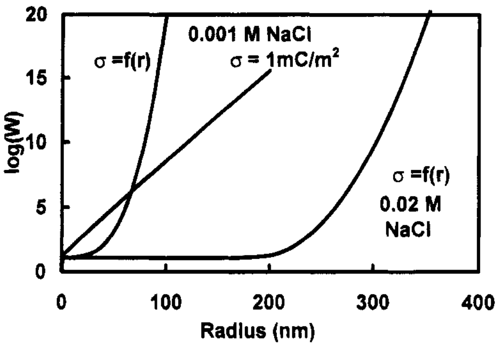

Figure 8. Stability ration, W, plotted as a function of copolymer particle radius, r, for two salt concentrations. W was calculated by numerically integrating eq 2 between 0.1 and 100 nm. For the two curves where charge density, σ, was a function of r, it was assumed that the mole fraction of DADMAC units in the copolymer was 0.0001, every DADMAC moiety contributed to the particle surface charge density, and the molar volumes of the DADMAC and the NIPAM units in the copolymer chain were 100 and 106 mL/mol, respectively. The Hamaker constant was assumed to be 8×10^{-21} J.

Particles were assumed to be spheres of copolymer containing two bound water molecules per amide group.[4] Furthermore, it was assumed that all the cationic groups were located at the interface or it was assumed that the surface charge density was constant. Corresponding surface potentials were calculated from the Gouy–Chapman theory and the potential energies of interaction were calculated from the following equation which includes the nonretarded Hamaker expression and the expression for electrostatic repulsion given by Buscall and Ottewill.[26]

$$P = \frac{-Ar}{12h} + 2\pi\Psi^2 r \ln(1 + \exp(-\kappa h)) \qquad (1)$$

where P is the total potential energy of interaction, A is the combined Hamaker constant, which was assumed to be 8×10^{-21} J, r is the particle radius, h is the surface-to-surface particle separation distance, ψ is the surface potential, and, κ is the Debye–Hückel parameter. The corresponding stability ratios were calculated from the following expression, which was evaluated numerically.

$$W = 2r\int_0^{\infty}\frac{\exp(P)}{h^2}\,\mathrm{d}h \qquad (2)$$

Stability ratios are shown as functions of particle radius and salt concentration in Figure 8. The curve showing the effect of constant surface charge density on log(W) versus r was nearly linear. By contrast, in the case of both curves denoting variable surface charge density, the stability ratios had constant low values for small particle sizes while increasing dramatically at larger particle sizes. Thus, we conclude that homogeneous nucleation is more likely to give a uniform particle size distribution when the charge groups concentrate at the particle–water interface because the stability ratio is a much stronger function of radius.

Many assumptions were made in calculating the curves in Figure 8. For example, the copolymer Hamaker constant was arbitrarily assigned. Nevertheless, the curves have qualitative value in illustrating our interpretation of the copolymer particle nucleation mechanism. For example, if the criterion for colloidal stability is arbitrarily considered to be $\ln(W) > 5$, then the minimum radius for colloidal stability is about 60 nm in 0.001 M NaCl compared with 270 nm in 0.02 M NaCl. Thus, precursor particles had to agglomerate to a higher degree to give larger particles in the higher ionic strength environment.

The results in Figure 6 showed that the size of phase-separated copolymer particles was temperature dependent. We believe that the different particle sizes reflect the different number of polymer chains per particle and not necessarily a change in swelling. Thus, the final particle diameter reflects the kinetics of nucleation and growth to form stable colloidal particles. We propose that near the CPT precursor particles form relatively slowly so the dominant process is the coagulative growth of existing particles. On the other hand, at higher temperatures the rate of precursor particle nucleation rate is greater so the final particle size is lower for a constant mass concentration of copolymer.

Conclusions

The main conclusions of the work are as follows:

1. NIPAM monomer is more reactive in aqueous free-radical polymerizations than DADMAC, giving broad molecular weight and composition distributions from batch polymerization.
2. The DADMAC/NIPAM copolymer aqueous solutions phase separated upon heating and the phase separation temperature was a slightly decreasing function of salt concentration.
3. Phase-separated copolymer is present as cationic colloidal particles which are electrostatically stabilized.
4. The dependency of the colloidal particle size was explained by a coagulative nucleation mechanism in which globules, formed from the collapse of copolymer coils, aggregated to give stable colloids.

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References and Notes

(1) Schild, H. G. *Prog. Polym. Sci.* **1992**, *7*, 163.
(2) Osada, Y.; Ross-Murphy, S. B. *Sci. Am.* **1993**, *268* (5), 82.
(3) Guillet, J. E.; Heskins, M.; Murray, D. G. U.S. Patent 4,536,294, 1985.
(4) Dong, L. C.; Yan, Q.; Hoffman, A. S. *J. Controlled Release* **1992**, *19*, 171.
(5) Schild, H. G.; Tirrell, D. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 342.
(6) Schild, H. G.; Tirrell, D. *Langmuir* **1991**, *7*, 905.
(7) Chiklis, C. K.; Grasshoff, J. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 1617.
(8) Priest, J. H.; Murray, S. L.; Nelson, R. J.; Hoffman, A. S. In *Reversible Polymeric Gels and Related Systems*; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987; p 255.
(9) Taylor, L.; Cerankowski, L. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2551.
(10) Pelton, R. H.; Chibante, P. *Colloids Surf.* **1986**, *20*, 247.
(11) Snowden, M. J.; Vincent, B. *J. Chem. Soc., Chem. Commun.* **1992**, 1103.
(12) McPhee, W.; Tam, K. C.; Pelton, R. H. *J. Colloid Interface Sci.* **1993**, *156*, 24.
(13) Tanaka, H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 29.
(14) Kokufuta, E. *Macromolecules* **1979**, *12*, 350.
(15) Alexandrowicz, Z. *J. Polym. Sci.* **1959**, *40*, 91.
(16) Richards, E. G. *An Introduction to the Physical Properties of Large Molecules in Solution*; Cambridge University Press: New York, 1980.
(17) Nagasawa, M. T.; Takahashi, A. In *Light Scattering from Polymer Solutions*; Hunglin, M. B., Ed.; Academic Press: London, 1972.
(18) Pelton, R.; Miller, P.; McPhee, W.; Rajaram, S. *Colloids Surf.* **1993**, *80*, 181.
(19) Tanaka, H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 29.
(20) Baade, W.; Hunkeler, D.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1989**, *38*, 185.
(21) Tam, K. C.; Ragaram, S.; Pelton, R. H. *Langmuir* **1994**, *10*, 418.
(22) Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26*, 5045.
(23) Meewes, M.; de Silva, M.; Nyffenegger, R.; Binkert, Th. *Macromolecules* **1991**, *24*, 5811.
(24) Feeney, P. J.; Geissler, E.; Gilbert, R. G.; Napper, D. H. *J. Colloid Interface Sci.* **1988**, *121*, 508.
(25) Goodwin, J. G.; Ottewill, R. H.; Pelton, R. H.; Vianello, G.; Yates, D. E. *Br. Polym. J.* **1978**, *10*, 173.
(26) Buscall, R.; Ottewill, R. H. In *Polymer Colloids*, Buscall, R., Corner, T., Stageman, J. F., Eds.; Elsevier: Amsterdam, 1985.

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