Colloid Polym Sci (2004) 282: 256–263
DOI 10.1007/s00396-003-0901-6

ORIGINAL CONTRIBUTION

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N-Vinylformamide as a route to amine-containing latexes and microgels

Received: 14 November 2002
Accepted: 6 March 2003
Published online: 6 May 2003

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Abstract Amine-containing poly(*N*-isopropylacrylamide) (PNIPAM) microgels and polystyrene-core-polyvinylamine-shell latexes were prepared by copolymerization with *N*-vinylformamide (NVF) followed by acid hydrolysis. Semi-batch methods were required to incorporate NVF into the gels or onto the latex. This requirement is in contrast to the behavior of acrylamide, which is an isomer of NVF and has similar polymerization rate constants in water. The highest yields of incorporated NVF were less than 50% for both microgels and latex. It is proposed that NVF does not partition as much as acrylamide in the PNIPAM particles during polymerizations. In the case of the PS latex, it is proposed that poly(*N*-vinylformamide) (PVNF) formed in solution is not very susceptible to hydrogen abstraction, which is necessary to form polystyrene grafted-PVNF.

The formamide moieties in the microgels and latex shells were converted to amine groups by acid hydrolysis. However, we were unable to achieve more than 50% hydrolysis. Thus, NVF is a route to amine-containing gels and amine-coated polystyrene particles, however, the reactions are not efficient.

Keywords Latex particles · *N*-Vinylformamide · Styrene · Amino groups · Surfactant-free emulsion polymerization

Introduction

Following a decade of activity in the patent literature [1, 2], *N*-vinylformamide (NVF) is now being produced in commercial scale quantities. NVF, an isomer of acrylamide, is of interest because it has low toxicity (unlike acrylamide) and high reactivity for homo- and copolymerization [3]. In addition, NVF moieties in polymers can be hydrolyzed to yield amine groups. For example, PNVF readily hydrolyzes under acidic or basic conditions to give poly(vinylamine-co-vinylformamide). Indeed, with enough patience, hydrolysis will yield pure polyvinylamine [4]. The poly(vinylamine-co-vinylformamide) family of copolymers has recently been commercialized by BASF.

Latex particles and microgels functionalized with primary amines are of interest because amines are readily derivatized with functional molecules including peptides, enzymes, and fluorescent groups. There are commercial vinyl monomers containing primary amines such as allylamine, however, NVF based systems may offer unique opportunities because there are no electrostatic effects complicating the polymerization.

In this work we report on our attempts to employ NVF-based approaches to the preparation of two types of amine-containing model colloids—monodisperse polystyrene latex [5] and amine-containing poly(*N*-isopropylacrylamide) (PNIPAM) microgel suspensions [6]. Before describing our work, it is relevant to review some

of the major existing approaches to the preparation of amine-containing particles and gels.

An obvious route to amine functional particles and microgels is via amine-containing monomers. For example, Delair et al. recently [7] described the surface functionalization of two colloidal systems—polystyrene latex particles with vinylbenzylamine and colloidal PNIPAM gels with 2 aminioethylmethacrylate. This follows the work of Homola and James who were one of the first groups to describe the use of amino monomer (diethylaminoethylmethacrylate) in surfactant-free polystyrene latex [8]. Another example, which is very relevant to our work, was published by Serizawa et al. [9]. They described the preparation of functional polymer core-shell particles using a macromonomer of PNVF and styrene. Their strategy involved the preliminary synthesis of the PNVF macromonomer with a terminal methylstyrene. The macromonomer was subsequently copolymerized with styrene by dispersion polymerization.

Cationic polymers can function as stabilizers for latex preparations yielding colloids stabilized by adsorbed polymer. One of the last publications out of Vanderhoff's laboratory describes the use of poly[(vinyl alcohol)-co-(vinyl amine)] as a stabilizer for polystyrene latex [10]. They concluded that the stabilizer was physically adsorbed.

Our work is concerned with attempts to prepare and characterize NVF containing styrene latex particles and PNIPAM microgels by surfactant-free (or almost free) emulsion polymerization. After the second stage polymerization, the composite particles and microgels were hydrolyzed with hydrochloric acid at 70 °C in order to obtain amino groups. The particles were characterized by dynamic light scattering, potentiometric and conductometric titration, and electrophoretic mobility.

Experimental

Materials

Styrene (Aldrich) and *N*-vinylformamide (Aldrich) were distilled under vacuum and stored at –15 °C prior to use. The initiator, 2, 2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (Aldrich), was recrystallized from water and methanol. *N*-Isopropylacrylamide (Kodak) was recrystallized from a mixture of toluene and hexane. *N*-Vinylformamide (Mitsubishi Chemical) was distilled under reduced pressure before use. The cross-linker, *N, N*-methylenebisacrylamide (BA) (Kodak), and cetyltrimethylammonium bromide (CTAB) were used as received. Milli-Q water was used in the polymerizations.

Preparation of polystyrene latex

Polymerizations were carried out in a 250 mL 3-necked round bottom flask equipped with a Teflon blade-type stirrer (200 rpm), condenser, and nitrogen inlet. The reaction temperature was controlled at 70 °C.

Polystyrene (PS) latex was prepared by a surfactant-free batch process following the recipe described by Goodwin et al. [11]. The reaction flask was charged with water (100 mL) and styrene (10 mL), purged with nitrogen and allowed to reach thermal equilibrium at 70 °C. An aqueous solution of the AIBA (0.09 g in 1 mL) was then added. The polymerization was carried out for 17 h. The resulting latex was filtered through glass wool to remove coagulum and then purified by successive centrifugation–decantation–dispersion cycles. The polymerization conversion was 70% and was determined gravimetrically. A 10 mL aliquot was taken for characterization, Sample L1, and the remaining amount (100 mL) was used as a seed for the second stage polymerization of NVF both in the presence and in the absence of a cross-linking agent.

Preparation of amino polystyrene latex

PS latex (50 mL, 1% w/w) and NVF (0.5 mL) were purged with nitrogen and allowed to reach thermal equilibrium at 70 °C. An aqueous solution of the AIBA (0.05 g in 1 mL) was then added. The polymerization was carried out for 2 h. The resulting latex, Sample L2, was purified by successive centrifugation–decantation–dispersion cycles. The same procedure was followed for the preparation of cross-linked latex particles, Sample L3, but in this case BA (0.05 g) was added to the PS latex and NVF mixture.

For the hydrolysis of L2 and L3, concentrated hydrochloric acid 5 M (0.3 mL) was added to the PVNF-containing styrene latex (10 mL). The mixture was purged with nitrogen and stirred at 70 °C for 24 h. The samples were purified by three successive centrifugation–decantation–dispersion cycles (Beckman GS-15R centrifuge, 8900 rpm and 30 min at 8 °C) yielding Samples L4 and L5 respectively.

Synthesis of NIPAM/NVF copolymer microgel

Initial attempts to prepare NVF-co-NIPAM microgels were by batch polymerizations. In a typical experiment 1.400 g NIPAM, 0.100 g NVF, 0.095 BA, and 0.050 g CTAB were dissolved in 155 mL water. The mixture was heated to 70 °C and purged with nitrogen for 1 h, after which 0.067 g initiator (AIBA) dissolved in 5 mL water was injected into the reaction mixture. The polymerization was stopped after 6 h. In every case, most of the microgel was coagulated.

In a typical semi-batch polymerization, 0.159 g NIPAM, 0.100 g NVF, 0.011 g BA, and 0.050 g CTAB dissolved in 125 mL water, were added to a 250 mL 3-necked flask in an oil bath at 70 °C and fitted with a mechanical stirrer. The mixture was purged with nitrogen for 1 h and 0.067 g initiator (AIBA) dissolved in water was injected into the reaction mixture to start the polymerization. After 20 min, the remaining monomer (1.241 g NIPAM and 0.084 g BA, dissolved in 30 mL water) was pumped into the reaction at a rate of 1 mL/min using a REGLO-Digital peristaltic pump. Microgels were hydrolyzed at pH 1.5 and 70 °C for 24 h.

The polymerization was terminated after 6 h. The final microgel latexes were stable and the suspension was nearly transparent with a slight blue color.

All microgel latexes were cleaned by five serum replacements using a Beckman model L7 ultracentrifuge with a TI60 rotor which was operated at 40 000 rpm for 90 min. The final conductivity of supernatant was less than 5 μS/cm.

Solution copolymerizations of NIPAM and NVF were performed to estimate the reactivity ratios. An aqueous solution of 0.355–3.195 g NVF and 5.093–0.565 g NIPAM in 95 mL water was polymerized at 50 °C using 6.8 mg AIBA initiator in 5 mL water. The polymerizations were stopped after 10–25 min and the

resulting polymer solution was dialyzed against deionized water for 10 days at room temperature. The purified polymer solution was freeze-dried and conversions were determined gravimetrically.

Characterization

Particle sizes were measured by dynamic light scattering using a Lexel laser (wavelength 514 nm) equipped with a BI-9000 AT digital correlator (Brookhaven Instruments). The scattering angle was 90° and the particle sizes were calculated using the non-negatively constrained least squares (regularized) method employing software BI9000AT version 6.1. The samples were diluted in KCl aqueous solution (0.001 mol/L) to permit measurements at different pH values with approximately constant ionic strength.

Potentiometric and conductometric titrations were carried out using a PC-Titration Plus (Man-Tech) and a conductivity meter (Man-Tech). Samples were prepared using an aqueous solution of NaCl (0.001 mol/L). Generally the particle concentration was in the range of 0.4 g/L for PS latex and 1 g/L for PNIPAM. NaOH (0.1 mol/L) was added first. The forward titration was stopped at pH 10.5; HCl (0.1 mol/L) was then added and the back titration was stopped at pH 3.

The electrophoretic mobility measurements were carried out in a Zeta potential analyzer (Brookhaven Instruments) at room temperature using the ZetaPals software. The samples were prepared by dispersing 1 drop of the latex into aqueous NaCl (0.001 mol/L, 20 mL) affording a concentration in the range of 100 to 200 mg/L. The pH was adjusted with HCl and NaOH.

Proton ^{1}H NMR spectra were recorded on Bruker AV-200 spectrometer at 200 MHz. D_2O was used as solvent and the residual H_2O signal at 4.72 ppm was used as an internal reference. The mole percentage of the *N*-vinylformamide in the microgel was determined from the ratio of the normalized integral of the amide group of NVF and the methyl group of NIPAM in the NMR spectra.

Results

Polystyrene-core-PVAm shell latex

Initial attempts to prepare surfactant-free polystyrene (PS)-core poly(*N*-vinylformamide)-shell (PS-PNVF) composite latex particles in a one-stage polymerization failed because of aggregation at high conversion. Instead, PS-PNVF composite latex particles were prepared by two-stage polymerizations. Some properties of the resulting latexes are summarized in Table 1. A polystyrene core latex was grafted with either PNVF (L2) or crosslinked PNVF (L3) which were hydrolyzed to give Samples L4 and L5, respectively.

Styrene was first polymerized for 17 h, then NVF was added and the reaction mixture was allowed to react for another 2 h. We propose that poly(*N*-vinylformamide) formed in the aqueous phase and then adsorbed onto the PS seed particles. In an effort to prevent desorption of PNVF in the hydrolysis step, Sample 3 was prepared with the cross-linking agent BA. L2 and L3 were hydrolyzed with hydrochloric acid yielding amino-containing polystyrene latex particles, i.e., L4 and L5, respectively.

Table 1 Average diameter and particle diameter of PS-PNVF composite latex at pH 7 in 1 mmol NaCl

Sample	Description	Dh (nm)	Electrophoretic mobility at pH 7, 1 mM NaCl ($m^2/Vs \times 10^8$)
L1	PS	341	2.54
L2	PS-g-PNVF	391	1.25
L3	PS-g-PNVF-co-BA	400	1.23
L4	Hydrolyzed L2	450	3.82
L5	Hydrolyzed L3	420	4.33

The derivatization of the latex particles was followed by titration, and measurement of particle size and electrophoretic mobility. The results are summarized in Table 1. Without BA, the hydrated PNVF corona was about 25 nm thick whereas the crosslinked corona was about 5 nm thicker. The electrophoretic mobilities of L2 and L3 were less than L1, the starting latex, because nonionic PNVF layer shifted the shear plane out from the charged polystyrene surface. After hydrolysis, the mobility values were highly positive indicating the presence of amine groups in the corona.

Figure 1 shows the average diameter and electrophoretic mobility of PS-g-PVAm latexes, L4 and L5 at three pH values. Latex L5, with the thicker cross-linked shell before hydrolysis (see L3 in Table 1), upon hydrolysis did not expand as much as L4 indicating that the crosslinks limited swelling of the PVAm corona. Both latexes got smaller as the pH was raised because the PVAm shell shrank when it was uncharged at high pH. The electrophoretic mobility curves were similar for L4 and L5 and the mobility was maximum at pH 7. Similar behavior was observed for microgel H4 at low temperature.

The PVAm shell latexes were negatively charged at pH 11 (see Fig. 1) indicating that not only were the

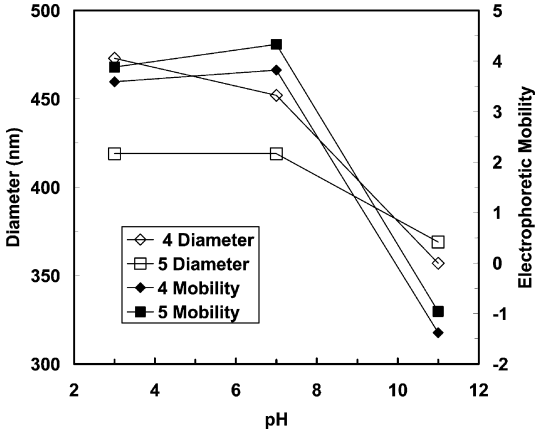

Fig. 1 Electrophoretic mobility and hydrodynamic diameter of PS-core-PVAm shell latexes L4 and L5

amines completely deprotonated, but that there must also be carboxyl groups in the latex shell, perhaps from the hydrolysis of terminal amidine groups [11].

NIPAM/NVF copolymer microgels

PNIPAM microgel latexes are generally prepared by a batch surfactant-free emulsion polymerizations[12]. In early experiments NVF was incorporated into batch NIPAM polymerization—see the B series in Table 2. The one-shot dispersions were not stable; B3, the highest NVF concentration, was completely coagulated. NMR analysis of the product revealed no detectable NVF moieties in the polymer (see B series in Table 3).

An obvious explanation for the poor batch polymerizations was that reactivity ratios were unfavorable for the formation of random copolymers. In order to estimate the reactivity ratios, a series of copolymerizations (no BA crosslinker) was conducted in aqueous solution at 50 °C using 0.1 mol% AIBA as an initiator. The copolymerization reactivity ratios of NIPAM with NVF were determined from the feed ratios of comonomers and resultant copolymer composition of low (i.e., $<15\%$) conversion samples using both the Fineman-Ross [13] and Kelen-Tudos [14] methods. The reactivity ratios for NIPAM and NVF are reported in Table 4. The value of r_{NIPAM} is close to 1.0 and much higher than that of r_{NVF} (0.09). Note that these polymerizations were not homogeneous so the validity of using overall monomer concentrations for estimating reactivity ratio is debatable. Nevertheless, these values are similar to the values for the homogenous polymerization of acrylamide and NVF reported by Kathmann and McCormick in 1993 [15]. Based on NVF/NIPAM reactivity ratios, NVF should easily be incorporated into the microgel. Perhaps the presence of BA cross-linker interferes with NVF incorporation.

Table 2 Microgel synthesized at 70 °C for 6 h. The continuous feed rate was 1 mL/min and began 20 min after the initiator was added

Sample		NIPAM (g)	BIS (g)	AIBA (g)	NVF (g)	CTAB (g)
C1	Initial charge	0.080	0.005	0.067	0.050	0.050
	Continuous feed	1.320	0.090			
C2	Initial charge	0.120	0.008	0.067	0.075	0.050
	Continuous feed	1.280	0.087			
C3	Initial charge	0.159	0.011	0.067	0.100	0.050
	Continuous feed	1.241	0.084			
C4	Initial charge	0.335	0.022	0.067	0.210	0.050
	Continuous feed	1.065	0.073			
NIPAM batch		1.400	0.095	0.067	0.000	0.050
B1 batch		1.400	0.095	0.067	0.050	0.050
B2 batch		1.400	0.095	0.067	0.100	0.050
B3 batch		1.400	0.095	0.067	0.210	0.050

Table 3 NVF contents of the first stage of copolymer microgel polymerizations and in the product as measured with ^{1}H NMR

Microgel	Mole of NVF in feed (M)	NVF in feed (M%)	NVF in microgel (M%)
NIPAM	0	0	0
B1	7.04×10^{-4}	5.1	0
B2	1.41×10^{-3}	9.8	0
B3	2.96×10^{-3}	18.5	0
C1	7.04×10^{-4}	5.1	2.6
C2	1.06×10^{-3}	7.5	3.8
C3	1.41×10^{-3}	9.8	5.8
C4	2.96×10^{-3}	18.5	10.8

Table 4 Reactivity ratios for copolymerization of NVF with NIPAM in water at 50 °C using 0.1 mol % AIBA as an initiator

	Fineman-Ross	Kelen-Tudos
r_{NVF}	0.081 ± 0.004	0.092 ± 0.037
r_{NIPAM}	0.85 ± 0.083	1.11 ± 0.147

A semi-batch synthesis was developed in which the initial charge consisted of all the NVF, an equimolar amount of NIPAM and 5 mol% BA of NIPAM (Table 2). After 20 min the remaining NIPAM and BA, dissolved in 30 mL water, were added by a peristaltic pump at a rate of 1 mL/min. Stable microgel suspensions were obtained and slightly more than one half of the added NVF was incorporated into the microgel particles (see Table 3).

The hydrolysis of copolymer microgels was carried out at pH 1.5, 70 °C for 24 h. The degree of hydrolysis of the microgels was calculated from the NMR spectra of microgels and the results are summarized in Table 5. Between 30 and 40% of the NVF moieties in the gels were converted to amines. It has been reported that it is difficult to obtain high hydrolysis conversions with PNVF homopolymer, presumably because the presence of charged amine groups inhibits the approach of acid catalyst to neighboring formamide groups.[4]

Table 5 Analysis of microgels for the hydrolysis of *N*-formamide groups to primary amines. The H series corresponds to the C series, after hydrolysis

Microgel	NVF in microgel (M%)	Amine mole fraction by NMR	Hydrolysis degree by NMR (%)	Amine mol% by titration
H1	1.6	1.0	39	1.1
H2	2.3	1.5	40	1.9
H3	3.5	2.3	40	2.0
H4	7.5	3.3	32	3.8

Microgel particle size

One of the most spectacular properties of PNIPAM microgels is temperature-sensitive swelling, which is conveniently measured by dynamic light scattering. Figure 2 summarizes the copolymer size data as a function of the mol% NVF incorporated into the gel. At 50 °C the crosslinked polyNIPAM particles were shrunken. Figure 2 shows a slight increase in particle diameter at 50 °C with increasing NVF content. This could indicate the presence of more polymer per particle. However, it could also reflect increased swelling upon replacement of NIPAM with the more hydrophilic NVF moieties. Hydrolysis of the low NVF content samples did not give an increase in swelling, whereas NVF contents greater than 5% showed significant increases in swelling upon hydrolysis. Charged polyNIPAM gels generally are more swollen than uncharged ones [6].

At 25 °C polyNIPAM microgels were highly swollen. The size increased with NVF content and further increased slightly when some of the NVF groups were converted to amines. The charged gels were more swollen and were less temperature sensitive than the corresponding nonionic gels.

The diameter of amine-containing microgel H2 is shown as a function of temperature in Fig. 3. At high pH most of the amine groups were not protonated and the gel swelling versus temperature was essentially the same as conventional PNIPAM microgels [6]. Swelling increased slightly with decreasing pH because of the contribution of ammonium groups to the swelling. The volume phase transition temperatures, corresponding to the steepest portion of the curves in Fig. 3, were about 1 °C higher for pH 6.5 and 3 than for pH 10.5. Previously we showed that binding cationic surfactant to PNIPAM microgels increased swelling but had little effect on the volume phase transition temperature [16].

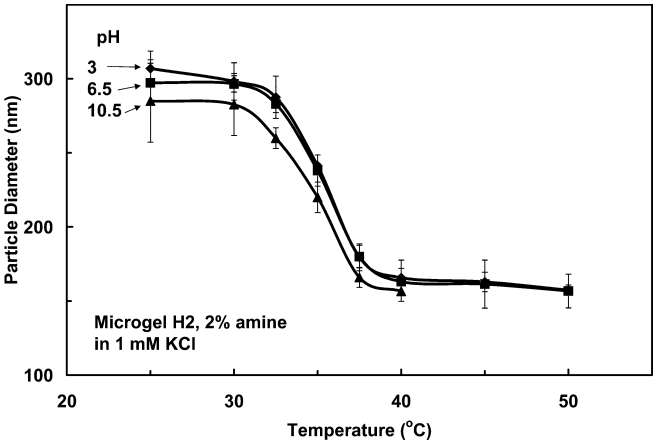

Fig. 3 Influence of temperature on the particle size of microgel H2

The swelling of amine-containing microgel is a function of the temperature, the amine content, and the pH. The effects of these three variables are illustrated in Fig. 4 and show diameter as a function of pH for two microgels at two temperatures. In general, swelling is much less sensitive to pH than to temperature, i.e., compare Fig. 3 and Fig. 4. Titration of polyvinylamine homopolymer shows a large polyelectrolyte effect which causes the charge content to decrease almost linearly over the whole pH range [17]. H4, the microgel with the highest amine content, showed the greatest sensitivity to pH. It is interesting that the pH sensitivity was also apparent at 50 °C where we might expect the gels to be dehydrated and rather insensitive to pH.

Electrophoretic mobility of microgels

PNIPAM microgels are known to have fascinating temperature-sensitive electrophoresis behavior [18]—when

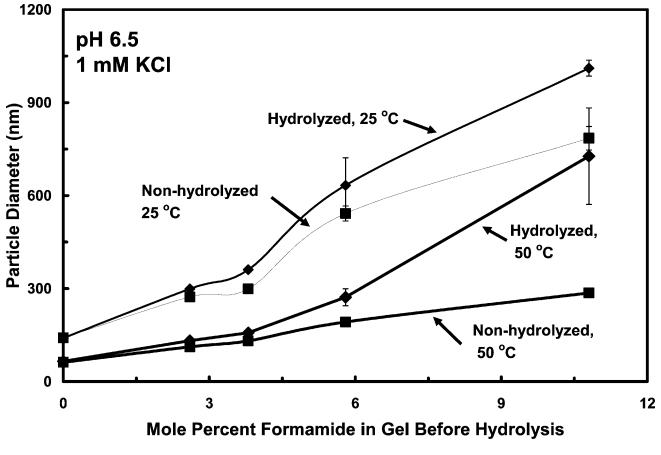

Fig. 2 PNIPAM-co-PNVF microgel latex diameter as a function of NVF incorporation in the gel

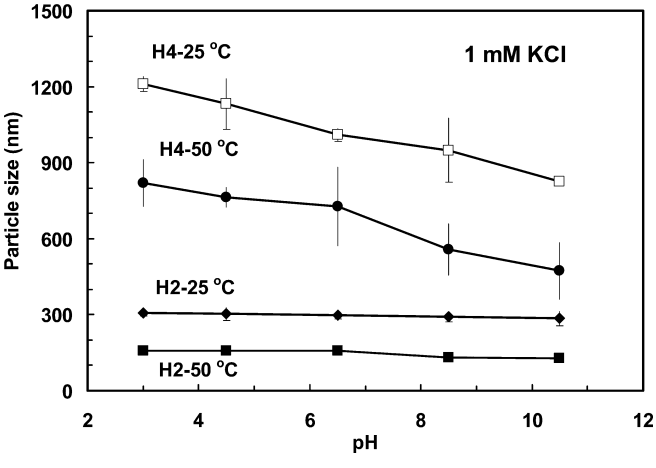

Fig. 4 Influence of pH and temperature on the swelling of behavior of two amine-containing microgels

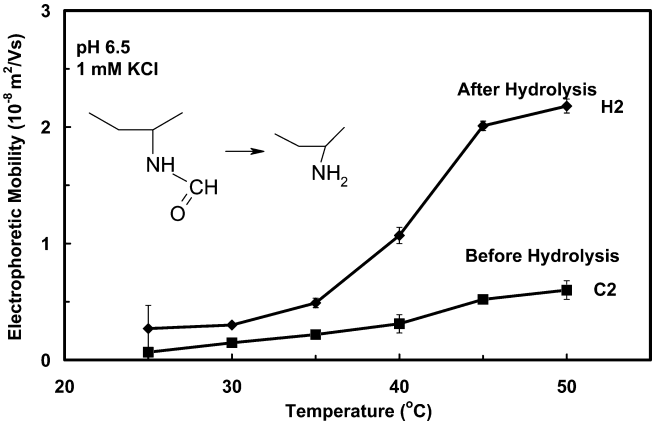

Fig. 5 Mobility as a function of temperature before and after hydrolysis of the *N*-vinylformamide moieties to amines

swollen (low temperature) the gels have a low effective surface charge density values whereas at high temperature, the gels bearing a fixed number of covalently bonded charges have a high charge density and, thus, a high electrophoretic mobility. Figure 5 shows mobility as a function of temperature before and after hydrolysis. Microgel C2 (3.8 mol% formamide groups) had a very low mobility at room temperature; shrinking the gel with heating raised the mobility to about half a mobility unit which is lower than usually achieved with NVF-free gels. Cationic amidine end groups are the source of the cationic charge in the C2 microgels [11].

The microgels were hydrolyzed at pH 1.5, 70 °C for 24 h. There was some concern that these conditions might hydrolyze the amidine groups to amide [19] and/or hydrolyze NIPAM to acrylate groups. A control experiment was conducted in which a NVF-free microgel was exposed to hydrolysis conditions. Figure 6 shows the electrophoretic mobility versus temperature before and after hydrolysis. There was little difference; thus, it was concluded that unwanted hydrolysis of amidine or isopropylacrylamide groups did not occur.

Figure 7 shows the mobility of three microgels as a function of temperature at pH 3. All three microgels showed similar temperature sensitivity corresponding to the particle size sensitivity seen earlier (Fig. 3). The mobility curves shifted up with increasing amine content.

The influence of pH on the electrophoretic mobility is summarized in Fig. 8. At high temperature, the mobility decreases monotonically with increasing pH due to the deprotonation of amine groups. On the other hand, the high temperature results were surprisingly insensitive to the NVF content. Microgel H1 with 1.0 mol% amine fell on the same curve as microgel H4 with 3.3 mol% amine. This suggests perhaps that the surface was saturated with amine groups in both cases.

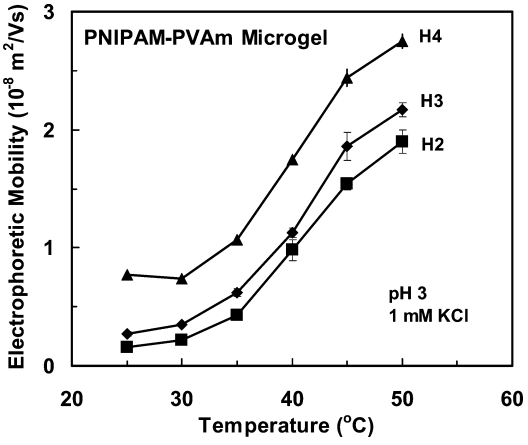

Fig. 7 Influence of temperature on the electrophoretic mobility of amine-containing PNIPAM microgel

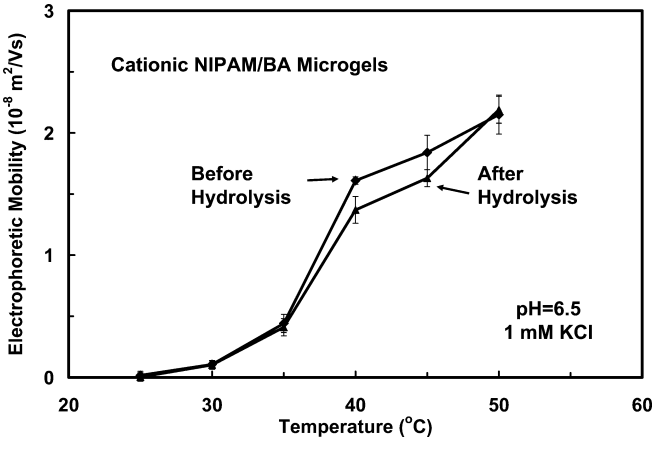

Fig. 6 Electrophoretic mobility of PNIPAM microgel before and after hydrolysis

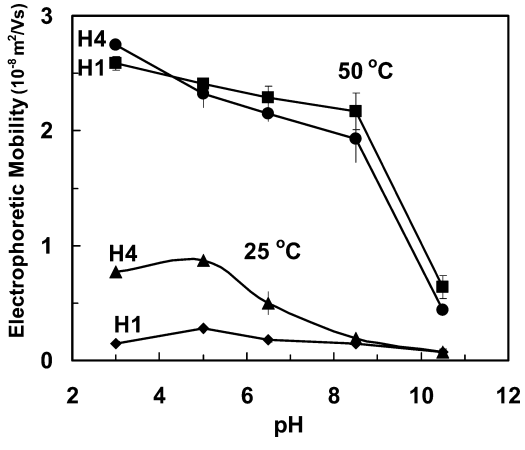

Fig. 8 Electrophoretic mobility of PNIPAM-PVAm microgel latex as a function of pH and temperature

At 25 °C, the microgels were water swollen and the higher amine content microgel H4 had higher mobility values and showed more pH sensitivity then did H1. The general features of the results in Fig. 8 are consistent with the reported behavior of cationic microgels [20].

Discussion

Both PNIPAM microgel and surfactant-free styrene polymerizations are precipitation polymerizations where the monomer is water soluble and the polymer is not. Of course, styrene is much more hydrophobic and much less soluble than NIPAM. There have been many reports showing that it is relatively easy to incorporate acrylamide into either PNIPAM [12] or PS latex [21]. In the case of NIPAM, the acrylamide copolymerization is believed to give a statistical distribution of acrylamide moieties in the gel. By contrast, surfactant-free styrene polymerizations in the presence of either acrylamide monomer or preformed polyacrylamide polymer produce PS particles with a polyacrylamide shell. These preparation recipes were the starting point for this work and we assumed that the NVF behavior would be similar to that of acrylamide. We were mistaken. For both PS latex and PNIPAM microgels, batch polymerizations did not yield monodisperse, colloidal stable dispersions. Many attempts were required to obtain semi-batch procedures which gave modest overall conversions of NVF to amine functionalized particles. Much of the added NVF was transformed into water-soluble products which were not characterized and which tended to aggregate the colloids. Reasons for this are now considered.

In the case of the polyacrylamide-g-polystyrene latex polymerizations, it is generally accepted that PAM formed in the aqueous phase adsorbs onto growing PS particles. Alternatively, the abstraction of a hydrogen from a PAM molecule in solution initiates styrene polymerization to form graft copolymer which adsorbs onto growing PS particles. The main evidence for this mechanism is:

1. PAM cannot be removed from the particle surfaces
2. Similar results are achieved in batch polymerizations starting either with added PAM or AM monomerWe propose that PVNF is less susceptible than PAM to hydrogen abstraction and thus less able to form styrene-grafted PVNF for particle stabilization.

The case of PNIPAM microgels is more difficult to explain. Why is it easy to incorporate AM in a simple batch polymerization whereas NVF requires careful semi-batch procedures? We can only speculate that NVF monomer does not partition into the collapsed PINIPAM gels during the polymerization—we have no evidence to support this explanation.

Another puzzling feature of these results concerns the difficulty in achieving high degrees of formamide hydrolysis. It is known that PNVF is increasingly difficult to hydrolyze under acidic conditions as the degree of hydrolysis increases. The usual explanation is that the positively charged cationic chain has a local pH value higher than that of the bulk solution due to the electrostatic repulsion of protons. However, as the overall content of formamide groups in the gel is low, it is surprising that this effect persists.

The behavior of both the aminated PS latex and the aminated PNIPAM microgel is consistent with similar particles produced by different routes. In particular, the PNIPAM showed a rich range of electrophoretic and swelling behaviors when temperature and pH were varied. Such systems have been described and modeled before [6].

Conclusions

1. It is possible to prepare amine-containing microgels and polystyrene latex by copolymerization with NVF and subsequent hydrolysis. However, in both cases the NVF incorporation and hydrolysis yields are less than 50%.
2. A semi-batch procedure in which NIPAM was fed into NVF was necessary to incorporate NVF into a colloidally stable product. NVF contents as high as 10.8 mol% were obtained, however, this represented only about 57% of the added NVF.
3. The relatively poor incorporation of NVF in both polystyrene and PNIPAM could not be explained by reactivity ratios. Instead, we propose that NVF is very hydrophilic and tends not to partition in growing particles.
4. Particle size of the NIPAM/NVF copolymer microgels increased with increasing NVF feed concentration. However, initial NVF concentrations greater than 7.5% gave broad particle size distributions and unstable microgel latex.
5. The acidic hydrolysis of the NIPAM/NVF microgel was also inefficient with a yield of approximately 39% .(Table 5). The resulting amine-containing microgel displayed temperature- and pH dependent swelling and electrophoretic mobility consistent with related PNIPAM systems described in the literature.
6. Although NVF is an isomer of acrylamide with similar polymerization kinetics, NVF is far more difficult to incorporate into surfactant-free polystyrene latex.

Acknowledgements Ana Barros-Timmons thanks the Fundação para a Ciência e Tecnologia (FCT) for the sabbatical grant. The Mechanical Wood-pulps NCE is acknowledged for Xu's support.

References

1. Linhart F, Degen H, Auhorn W, Kroener M, Hartmann H, Heide W (1988) US Patent 4,772, 359
2. Lai T (1990) Eur Patent Application 0264649
3. Kroner M, Dupis M, Winter M (2000) J Prakt Chem 342:115
4. Gu L, Zhu S, Hrymak A, Pelton R (2001) Polymer 42:3077
5. Goodwin J, Hearn J, Ho CC, Ottewill RH (1974) Colloid Polym Sci 252:464
6. Pelton R (2000) Adv. Colloid Interface Sci 85:1
7. Delair TH, Meunuier F, Elaissari M, Charles M, Pichot C (1999) Colloids Surf A 153:341
8. Homola A, James RO (1977) J Colloid Interface Sci 59:123
9. Serizawa T, Taniguchi K, Akashi M (2000) Colloids Surf A 169:95
10. Campbell KD, Sagl DJ, Vanderhoff JW (1998) J Disp Sci Tech 19:785
11. Goodwin J, Ottewill RH, Pelton RH, Colloid Polym Sci (1979) 257:61
12. Pelton R, Chibante P (1986) Colloids Surf 20:247
13. Fineman M, Ross SD (1950) J Polym Sci 5:259
14. Kelen T, Tudos F (1975) J Macromol Sci Chem A9:1
15. Kathman EEL, McCormick CL (1993) Macromolecules 26:5249
16. Tam KC, Ragaram R, Pelton RH (1994) Langmuir 10:418
17. Katchalsky A, Mazur J, Spitnik P (1957) J Polym Sci XXIII:513
18. Pelton RH, Pelton HM, Morphesis A, Rowell RL (1999) Langmuir 5:816
19. Wahl R, Zeng LS, Madison SA, DePinto RL, Shay BJ (1998) J Chem Society, Perkin Transaction 2 9:2009
20. Fernandez-Nieves A, Fernandez-Barbero A, Nieves L, Vincent B (2000) J Phys: Condensed Matter 12:3605
21. Kawaguchi H, Hoshino H, Ohtsuka Y (1981) J Appl Polym Sci 26:2015