

D. Duracher
A. Elaïssari
C. Pichot

Characterization of cross-linked poly(*N*-isopropylmethacrylamide) microgel latexes

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D. Duracher · A. Elaïssari · C. Pichot (✉)
Unité mixte CNRS-BioMérieux
Ecole Normale Supérieure de Lyon
46 Allée d'Italie
F-69364 Lyon cedex 07, France
e-mail: christian.pichot@ens-bma.cnrs.fr
Tel.: +33-4-72728364
Fax: +33-4-72728533

Abstract This article reports the colloidal and physicochemical characterization of crosslinked poly(*N*-isopropylmethacrylamide) (poly[NIPMAM]) latexes. The latex particles were first characterized by determining the lowest critical solubility temperature by measuring the optical density variation as a function of temperature. In addition, the electrophoretic mobility behaviors of all latexes were examined as a function of pH and temperature. Finally, the colloidal stability was

investigated by determining the critical coagulation concentration and the critical flocculation temperature, and the corresponding results were discussed by taking into account both the effect of salinity and temperature on the solvency of poly[NIPMAM].

Key words Poly(*N*-isopropylmethacrylamide) · Electrokinetic mobility · Colloidal stability · Critical coagulation concentration · Critical flocculation temperature

Introduction

In recent years, increasing attention has been focused both on the preparation and characterization of microgel latexes containing thermosensitive polymers. Much published work has dealt with both fundamental aspects and practical applications of such particles, mostly with poly(alkylacrylamide) derivatives such as poly(*N*-isopropylacrylamide) poly[(NIPAM)] [1–3], poly(*N*-ethyl-acrylamide) [4] or poly(alkylacrylate) [5–7].

The outstanding properties of these thermosensitive latexes were clearly evidenced, especially the drastic variation of their colloidal behavior (particle size, electrophoretic mobility, colloidal stability) upon raising the temperature above the lowest critical solubility temperature (LCST). As a result, many applications were developed to take advantage of such a property, especially in the biological field, where the hydrophilic–hydrophobic transition of the microgel particles at the LCST together with the swelling capacity variation explain the versatility of these applications.

For various purposes it might be appropriate to produce hydrogels exhibiting a different thermal behavior than poly(NIPAM) (LCST = 32 °C) since, for instance, many biological reactions must be performed at 37 °C. Therefore, the selection of microgel particles with a LCST greater than 37 °C might be suitable. Several routes were indeed explored for modifying the phase-transition temperature of poly(NIPAM)-based materials (either as macrogel or microgel particles): copolymerization of NIPAM with monomers exhibiting hydrophilic or hydrophobic character [8–13], adding an ionic surfactant such as sodium dodecylsulfate [2, 14–17], etc.

Among polyalkylmethacrylamide derivatives, poly(*N*-isopropylmethacrylamide) [poly(NIPMAM)] has a LCST between 38 and 44 °C [18–20] and in addition a hysteresis phenomenon of the transition has been observed [21–23].

In a recent paper [24], we reported the synthesis for the first time of such poly(NIPMAM) in a particulate form through a radical-initiated precipitation polymerization process in the aqueous phase. A thorough

kinetics study allowed the investigation of the influence of pertinent parameters (initiator and cross-linker concentrations, reaction temperature) on the polymerization rate, the particle size and the formation of water-soluble polymers. In all cases, the latexes produced exhibited a very narrow particle size distribution.

This paper reports the colloidal and physicochemical characterization of these novel poly(NIPMAM) microgel particles prepared under various experimental conditions. The variation of the particle size, the electrophoretic mobility behavior, the colloidal stability and the coil-to-globule transition have been investigated as a function of temperature and method of latex preparation.

Experimental

Materials

NIPMAM was synthesized using isopropylamine, methacryloyl chloride and anhydrous dioxane (from Aldrich, used as received) as already reported [24]. The monomer obtained was purified by repetitive recrystallization in a pentane/toluene mixture. Potassium persulfate (KPS) initiator (reagent grade from Prolabo) and methylene bisacrylamide (MBA) from Aldrich were used without further purification. Water was of Milli-Q grade (Millipore, France) and was boiled for 2 h under a nitrogen stream before use.

Methods

Preparation of poly[NIPMAM] latexes

Polymerization experiments were performed using the batch polymerization process. The details of the synthesis and the polymerization kinetics have been reported elsewhere [24]. Three series of latexes were prepared by investigating the following parameters on the polymerization kinetics and processes (for 1 g NIPMAM monomer):

1. The effect of temperature (60, 70 and 80 °C).
2. The effect of initiator (KPS) concentration (0.01–0.03 g)
3. The effect of cross-linker (MBA) concentration (0.02–0.2 g).

A brief summary of the polymerization recipes used for the latex synthesis is given in Table 1.

Characterization of latexes

All latexes described here were cleaned by repetitive centrifugation and redispersion using deionized and boiled water in order to remove free electrolytes and water-soluble polymers before any colloidal characterization.

Particle size and distribution. Particle size was measured by quasi elastic light scattering (QELS). The diameter was measured as a function of temperature from 10 to 60 °C and the values reported are the averages of at least six measurements. Samples were vacuum degassed to prevent bubble formation at elevated temperature. The QELS apparatus was a Zeta Sizer 3000 HS from Malvern Instruments (Malvern, UK).

Lower critical solubility temperature. The LCST of the latex particles was investigated by measuring the optical density of a highly diluted latex dispersion as a function of temperature (ranging from 20 to 60 °C) in given conditions (pH 6 and 10^{-5} M

Table 1 Summary of polymerization recipes used for latex preparation. Polymerization conditions: 50 ml boiled and deoxygenated water, constant agitation (200 rpm), polymerization time 6 h. Ingredients: *N*-isopropylmethacrylamide (NIPMAM), methylene bisacrylamide (MBA), potassium persulfate (KPS)

Run	NIPMAM (g l ⁻¹)	MBA (%w/w)	KPS (%w/w)	T (°C)
222	20	2	2	70
242	20	4	2	70
282	20	8	2	70
2122	20	12	2	70
2162	20	16	2	70
2202	20	20	2	70
281/2	20	8	0.5	70
281	20	8	1	70
283	20	8	3	70
2122 ⁶⁰	20	12	2	60
2122 ⁸⁰	20	12	2	80

NaCl). The optical density (OD) was measured using a $Uv=mc^2$ spectrophotometer (Safas, Monaco) at 500 nm. The heating rate was 0.2 K min⁻¹ and was kept constant during the experiment. The temperature was controlled when heating the polymer solution by using an internal heating system with an automatic control device. The LCST was then determined from the inflection point of the OD versus temperature curve.

Electrophoretic mobility. The electrophoretic mobility of the latexes was measured using a Zeta Sizer III, from Malvern Instruments. The electrophoretic mobilities were determined as a function of temperature at a constant pH (6.0) and at 10^{-3} M NaCl and as a function of pH below (20 °C) and above (50 °C) the LCST of poly[NIPMAM]. Each value was obtained by taking the average of at least three measurements.

Colloidal stability. The colloidal stability of the latexes was studied using the turbidity method (with a UVIKON 930 spectrophotometer). The latex dispersion was highly diluted in Milli-Q water at pH 6 at 20 °C. The coagulation rate constants were determined by measuring the OD variation (at 500 nm) as a function of time after adding NaCl solution. The critical coagulation concentration (ccc) of the latex particles was determined from the variation of the stability factor (W) as a function of ionic strength on a log–log scale. The stability factor was calculated using the following equation:

$$W = \frac{(\partial OD/\partial t)_f}{(\partial OD/\partial t)_s}, \quad (1)$$

where $(\partial OD/\partial t)_f$ and $(\partial OD/\partial t)_s$ are the initial slopes of the OD variation as a function of time (t) for fast and slow coagulation, respectively. More information concerning the experimental details and the theoretical background of colloidal stability are reported by Sonntag and Strenge [25].

The critical flocculation temperature (CFT) of poly[NIPMAM] latex at various concentrations of NaCl was determined by reading the absorbancy at 500 nm using a UV-vis spectrophotometer (SAFAS, Monaco). Poly[NIPMAM] latex was diluted in a given concentration of a NaCl solution at 25 °C. The temperature was gradually raised from 25 to 60 °C with a constant heating rate (0.2 K min⁻¹) during the experiment. The temperature was measured directly in the cell by using a thermocouple. The absorbancy measured was read as a function of temperature and the CFT was defined as the temperature where the absorbancy decreased.

Results and discussion

Characterization of latexes

Particle diameters were measured by quasielastic light scattering for highly diluted dispersions. As already reported by several authors [2, 26–28] the hydrodynamic particle size of poly[NIPAM] was found to be dependent on the nature and concentration of the electrolyte, the nature of the solvent, and the temperature. The variation of the hydrodynamic diameter as a function of temperature for poly[NIPMAM] latexes is reported in Fig. 1.

As expected, there is a large variation in particle diameter when the temperature of the medium is increased. Between 10 and 35 °C, the particle diameter decreases slightly or is almost constant considering the experimental errors. Such particle size variation is consistent with the increase in temperature that is sufficient to break some hydrogen bonds and reduce the hydrodynamic particle size but that is not enough to induce the coil-to-globule transition corresponding to a collapsed state.

Secondly, in the temperature range from 35 to 50 °C, particle size drastically drops with a constant slope due to shrinkage of the poly[NIPMAM] induced by the breaking of hydrogen bonds around NIPMAN between the polymer and water. This dehydration process leads to a coil-to-globule transition phenomenon; this has been extensively investigated and reported by several authors for alkylacrylamide derivatives, either for polymers in free solution [29] or for cross-linked polymers (macrogels and microgels) [30–32].

At upper temperatures, between 50 °C and 60 °C, a slight decrease in particle size is observed but is very difficult to determine accurately due to the fluctuation in the measurements in this temperature range. The final size observed at high temperatures is very near to the size determined by scanning electron microscopy when the particles are in their dry state.

The dramatic decrease in particle size observed for the poly[NIPMAM] particles is consistent with the reported values of the LCST for linear poly[NIPMAM]. Indeed, the reported values are between 38 and 47 °C depending on the experimental methods used for the determination of the LCST.

The particle sizes measured for all latexes are given in Table 2, and the difference (δ) between the particle size below and above the LCST is also reported. Several observations can be made:

1. The increase in cross-linker concentration (from 2 to 12%) decreases the swelling factor of the latex (this was attributed to a more cross-linked structure of the microgels). The apparent swelling factor increase for high MBA concentration might be due to a large error in the particle size analysis at 20 °C (and the

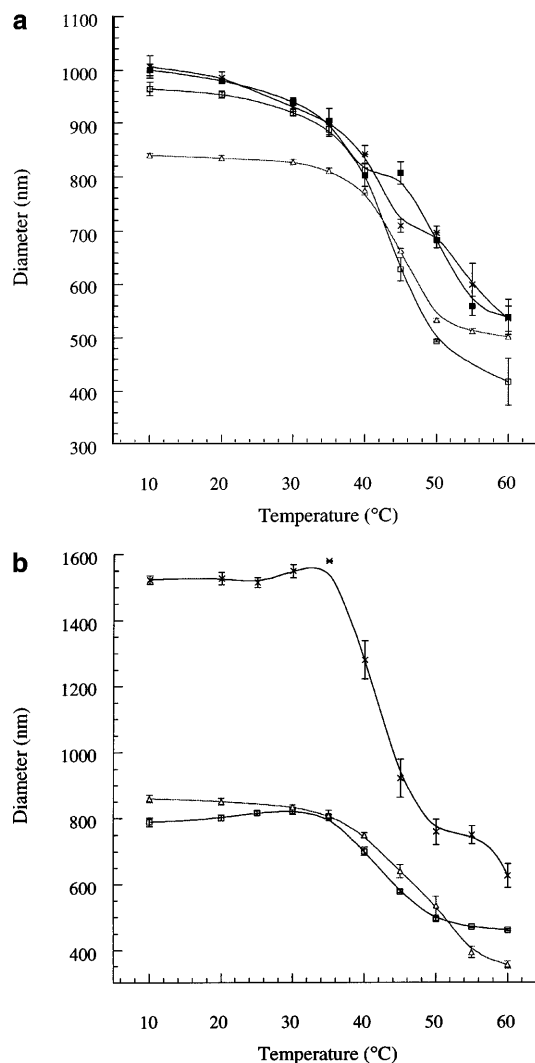


Fig. 1a, b Hydrodynamic diameter of poly(*N*-isopropylmethacrylamide) ■ latexes as a function of temperature. **a** Effect of cross-linker concentration: latex 242 (□), latex 282 (△), latex 2162 (■), latex 2202 (×). **b** Effect of polymerization temperature: latex 2122⁸⁰ (□), latex 2122 (△), latex 2122⁶⁰ (×)

possibility of the presence of a few associated particles).

2. Increasing the initiator concentration in the polymerization recipe also leads to a decrease in the swelling factor; this can be attributed to the formation of cross-linked poly(NIPMAM) chains.
3. The effect of temperature can be explained similarly, since increasing the temperature leads to an increase in radical formation.

All the swelling factor values should be taken with care due to the experimental error made in the particle diameter determination by QELS notably below the transition temperature where the particle size is larger than the laser wavelength.

Table 2 Particle size measured by quasielastic light scattering (at 20 and 50 °C) and by scanning electron microscopy (SEM)

Run	Diameter (nm) at 20 °C	Diameter (nm) at 50 °C	Thickness δ (nm) ^a	Diameter (nm) by SEM	Swelling factor $(D_{20^\circ}/D_{50^\circ})^3$
222	1030	446	292	400	12.3
242	1005	492	256	460	8.5
282	894	570	162	490	3.9
2122	900	580	160	510	3.7
2162	933	556	188	540	4.7
2202	1120	613	250	570	6.1
281/2	1020	492	264	460	8.9
281	999	533	233	514	6.6
283	937	550	193	570	4.9
2122 ⁶⁰	1530	643	693	680	13.5
2122 ⁸⁰	779	466	156	430	4.7

$$^a \delta = (D_{20^\circ} - D_{50^\circ})/2$$

Lower critical solubility temperature

The solubility of the poly(alkylacrylamides) and poly(alkylmethacrylamides) in water depends on the sidechain length of the alkyl groups as already stated by Ito [18]. Poly(alkylmethacrylamide) derivatives generally exhibit higher LCST than poly(alkylacrylamide) polymers having an identical sidechain [18, 21]. In the same series of polyacrylamide or polymethacrylamide derivatives having different alkyl groups, those with longer alkyl groups have lower LCST. This was explained by considering the increase in the hydrophobic character of the polymer, which causes a decrease in the solubility of the polymer in water through a modification of the balance between hydrogen-bond formation with water and intermolecular hydrophobic forces [33]. Reported values by different authors [18–23] are found to be between 38 and 47 °C for the phase separation of poly[NIPMAM] in aqueous solutions. The broad range of the quoted values of the LCST for poly[NIPMAM] may originate from the use of disparate methods for the determination of the transition, such as turbidity, differential scanning calorimetry, size-exclusion chromatography or light scattering. Netopilik et al. [22] proposed that the LCST is the highest temperature at which no phase separation is observed even after a very long time. In fact the authors found a transition temperature of 38 °C with an induction time of 8 h. Inomata et al. [34] determined the transition temperature from the intersection absorbancy point of the base line and the leading edge of the endotherm provided by differential scanning calorimetry measurements. However, several authors considered the LCST as the temperature at the inflexion point in the normalized absorbancy versus temperature curve.

The LCSTs of all latexes were determined by measuring the absorbancy of a highly diluted solution (at pH 6 in deionized water) as a function of temperature. The curves of the OD variation as a function of temperature obtained for all latexes are reported in normalized forms. Before any LCST determinations had been performed, it was postulated that the LCST for

hydrogel latexes corresponds to the inflexion point of the absorbancy variation versus temperature curve.

- As illustrated in Fig. 2a, which shows the normalized OD versus temperature, it can be pointed out that there is no significant effect of the initiator concentration on the LCST value. This can be explained by the slight influence of the initiator in the concentration range investigated on the structure of the particles such as the cross-linking density and the composition.
- The LCST was also measured for three latexes prepared at 60, 70 and 80 °C. All the LCSTs determined are near 40 °C irrespective of the polymerization temperature. The normalized OD variation as a function of temperature for this series of latex particles is reported in Fig. 2b. As discussed already, the observed behavior reflects a somewhat similar particle structure.
- In contrast, it seems that varying the cross-linker concentration (MBA) in the polymerization recipe significantly affects the phase-transition behavior of the corresponding final latexes (see Fig. 2c). As reported in Fig. 3, the LCST is found to decrease upon increasing the amount of cross-linker in the polymerization recipe, leading to LCSTs ranging from 38 to 45 °C. The observed behavior reflects the fact that the more cross-linked the particles, the broader the transition domain versus temperature. To some extent, the effect of MBA on the LCST can only be evidenced using the turbidity method as pointed out in this work and not using particle size variation as a function of temperature as reported by Mc Phee et al. [2] and Fujimoto et al. [33].

Electrokinetic study

The electrophoretic mobility (μ_e) for all latexes was investigated as a function of pH at 10^{-3} M NaCl at temperatures both below (20 °C) and above (50 °C) the

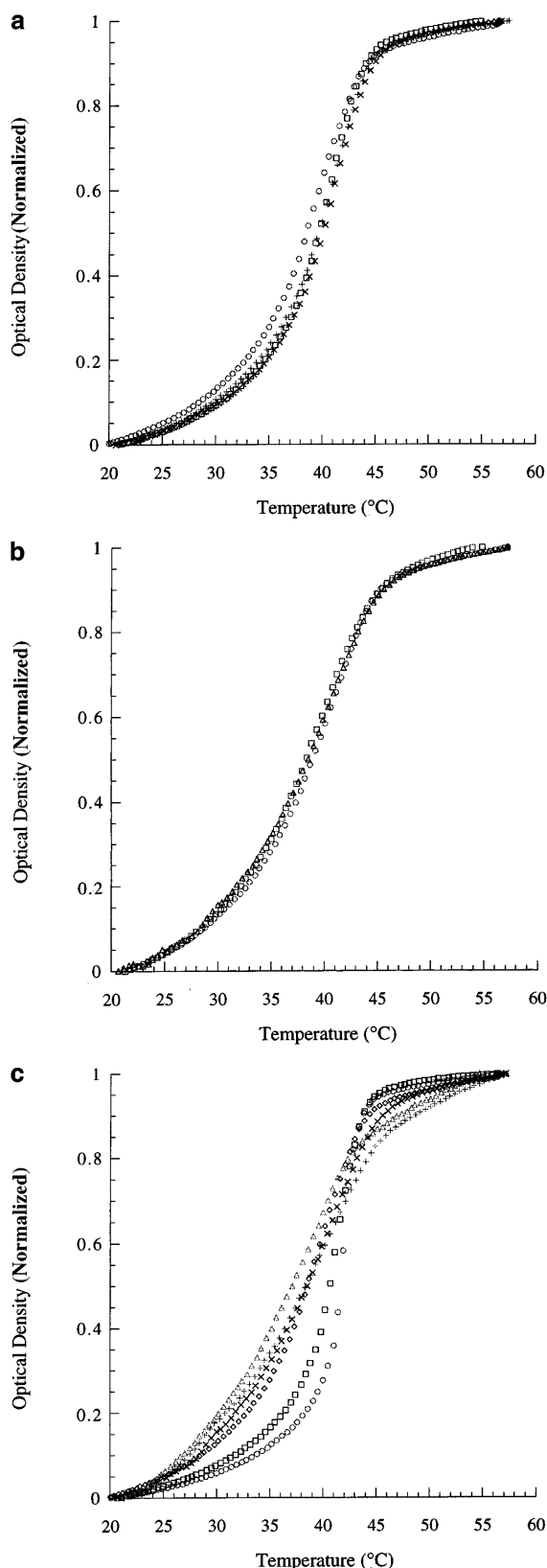


Fig. 2a–c Phase-transition curves of poly[NIPMAM] latexes. **a** Effect of initiator concentration: latex 281/2 (+), latex 281 (□), latex 282 (○), latex 283 (×) **b** Effect of polymerization temperature: latex 2122⁶⁰ (○), latex 2122⁷⁰ (△), latex 2122⁸⁰ (□) **c** Effect of crosslinker (methylene bisacrylamide): 222 (○), latex 242 (□), latex 282 (◇), latex 2122 (×), latex 2162 (+), latex 2202 (△) (only 20% of the data are represented on the figure)

LCST of poly[NIPMAM] polymers, and as a function of temperature at a constant pH (6.0) and ionic strength (10^{-3} M NaCl).

- Firstly, electrophoretic mobility was investigated as a function of pH in order to determine the effect of pH on the net surface charge density variation. As shown in Fig. 4a which reports the electrophoretic mobility variation versus pH at 20 °C for latex 282, a constant and negative electrophoretic mobility value is obtained in the pH range from 3 to 11, reflecting the negative and low surface charge density attributed to the presence of sulfate groups originating from KPS used as the initiator in the polymerization recipe. In contrast, the measured electrophoretic mobility as a function of pH above the LCST is found to be higher than that below the LCST and a negative value in the pH range is observed. In addition, the increase in the electrophoretic mobility below pH 5 can be assigned to the presence of carboxylic and hydroxyl end groups, due to possible hydrolysis and subsequent oxidation of the sulfate groups, a well-known behavior reported in the case of persulfate-initiated polymerization [35]. In all cases, the latexes investigated exhibit a negative electrophoretic mobility as a function of pH (from pH

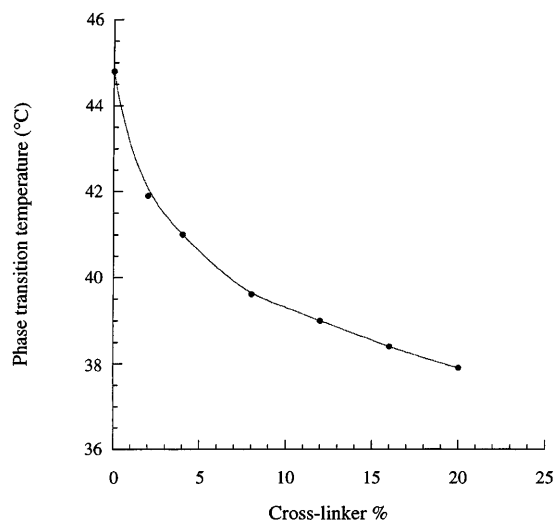


Fig. 3 Phase transition temperature lowest critical solubility temperature of poly[NIPMAM] latexes as a function of cross-linker concentration

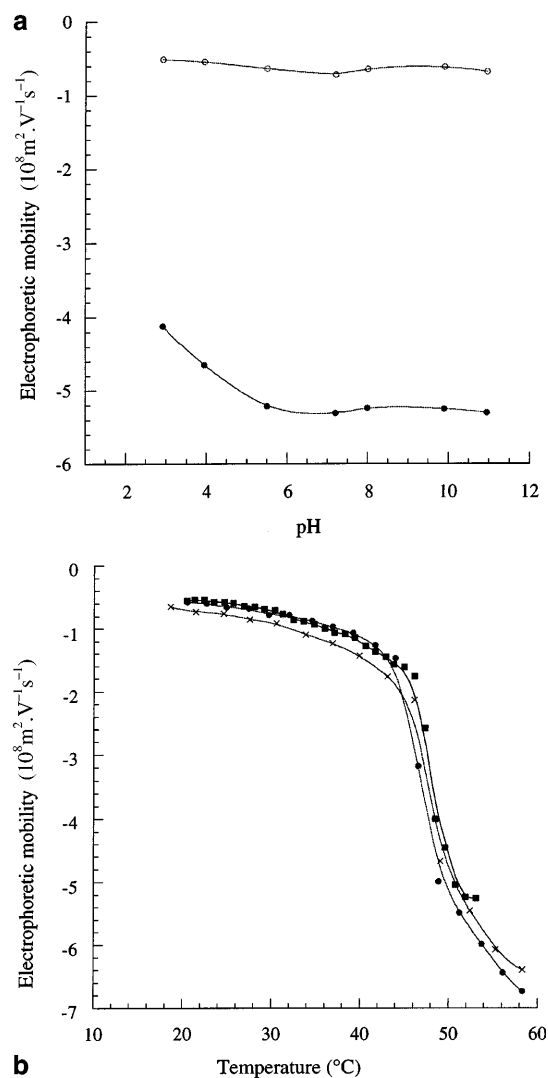


Fig. 4 **a** Electrophoretic mobility of poly[NIPAM] latex 282 as a function of pH at 20 °C (○) and at 50 °C (●). **b** Electrophoretic mobility of poly[NIPAM] latexes as a function of temperature: influence of initiator concentration. Latex 281/2 (●), latex 282 (■), latex 283 (×)

3 to 11) irrespective of temperature. The electrophoretic mobilities measured at pH 6 and 10^{-3} M NaCl are found to be close to $-0.6 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [except for runs 2202 (-1.3) and 2122⁸⁰ (-1.46), which are the more cross-linked and the smaller particles, respectively] at 20 °C and between -4.5 to $-5.5 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 50 °C. The slight difference in electrophoretic mobility for all the latexes can be attributed to some extent to a slight difference in the surface charge densities irrespective of the polymerization recipe. The electrophoretic mobilities measured at 20 and 50 °C are reported in Table 3.

- Secondly, the electrophoretic mobility was measured as a function of temperature at a constant pH of 6.0,

and at constant ionic strength (10^{-3} M NaCl). The results obtained for the three latexes are reported in Fig. 4b for illustration (samples prepared with various initiator concentrations). For all the latexes, the electrophoretic mobility is found to be negative. In addition, the electrophoretic mobility versus temperature curve, exhibits the same curvature profile irrespective of the method of latex preparation in the domain investigated for all reactants. Electrophoretic mobility indeed rises upon increasing the temperature as already reported by Pelton et al. [31] for microgel poly[NIPAM] particles. This observed behavior was explained by an increase in the surface charge density induced by the reduction in particle size due to the thermal sensitivity of such latex particles.

Colloidal stability

Critical coagulation concentration

The colloidal stability of latex particles was studied at pH 6 at 20 °C below the LCST of poly[NIPAM]. The ccc values deduced are reported in Table 3 for all latexes. In addition, the stability curves for a series of latex particles (effect of initiator concentration) are given in Fig. 5, in which the stability factor W (defined by Eq. 1) is reported as a function of electrolyte concentration (NaCl salt) on a log–log scale. Firstly, the ccc values obtained from the stability curve are much higher than for surfactant-free sulfate-charged polystyrene latexes [36, 37] the ccc values of which are generally near 0.1 M NaCl. This behavior can be attributed to the contributions of both the electrostatic stabilization and the steric stabilization [38–41] originating from the non-cross-linked interfacial polymer chains.

Table 3 Electrophoretic mobility μ_e below and above the lowest critical solubility temperature of poly[NIPAM] and the critical coagulation concentration (*ccc*) at 20 °C. Some data were not determined (*ND*)

Run	μ_e at 20 °C ($10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_e at 50 °C ($10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$)	ccc at 20 °C (mol l^{-1} NaCl)
222	ND	ND	ND
242	-0.71	-4.56	1.77
282	-0.59	-4.86	1.92
2122	-0.72	-4.41	1.99
2162	ND	ND	1.93
2202	-1.3	-5.67	1.8
281/2	-0.65	-5.29	1.84
281	ND	ND	1.84
283	-0.754	-4.97	1.94
2122 ⁶⁰	-0.77	-5.01	1.37
2122 ⁸⁰	-1.46	-5.5	1.9

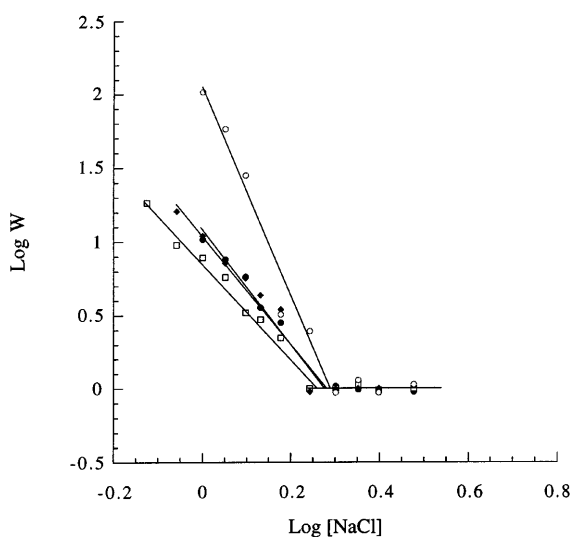


Fig. 5 Critical coagulation concentration of poly[NIPMAM] latexes at 20 °C: influence of initiator concentration on the stability factor: latex 281/2 (●), latex 281 (□), latex 282 (◆), latex 283 (○)

No significant difference in the ccc can be observed between all the samples, except for run 2122⁶⁰, but the large size of this latex may explain its low colloidal stability. This observation reflects the fact that these latexes are mostly sterically stabilized below the LCST and suggests that they exhibit almost the same colloidal stabilization irrespective of their interfacial polymer structure (charge density, swelling capacity and cross-linking density).

Critical flocculation temperature

The change in the OD of the dispersion as a function of temperature for different salt concentrations is illustrated in Fig. 6. In the absence of salt, a typical LCST curve is observed without any flocculation above the LCST. At low ionic strength (below 10^{-2} M NaCl) the transition temperature is always observable and no flocculation occurs and the LCST of the particles shifts slightly towards a lower temperature in this concentration range. At a higher ionic strength, (above 10^{-2} M NaCl) two phenomena are clearly evidenced. At first, the latex is no longer stable when the temperature is raised above the LCST of poly[NIPMAM] as observed in Fig. 6. Aggregation takes place when a large decrease in the OD is observed, corresponding to sedimentation of particles which is a consequence of particle flocculation. Secondly, the higher the salt concentration, the more rapidly the OD increases upon raising the temperature. In this range of salinity (above 10^{-2} M NaCl), the LCST temperature of the polymer is drastically dependent on the salt concentration as already observed by Snowden et al. [42] in the case of poly[NIPAM] latexes.

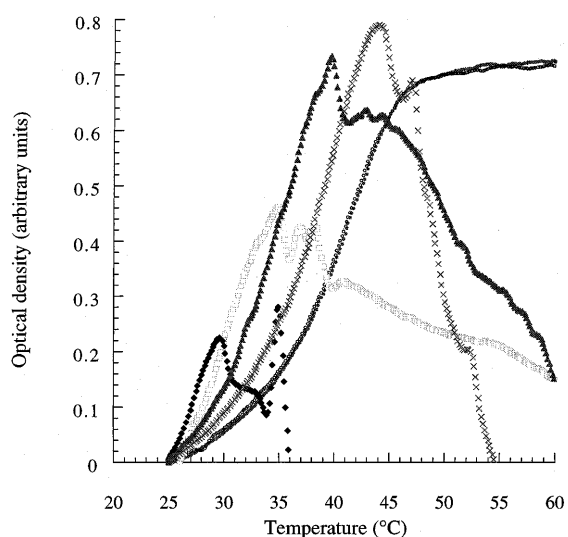


Fig. 6 Determination of the critical flocculation temperature (CFT) of poly[NIPMAM] latex 282 by measuring the variation in optical density as a function of temperature for different NaCl concentrations. 10^{-5} M (●), 10^{-2} M (○), 10^{-1} M (×), 5×10^{-1} M (▲), 1 M (□), 1.5 M (◆)

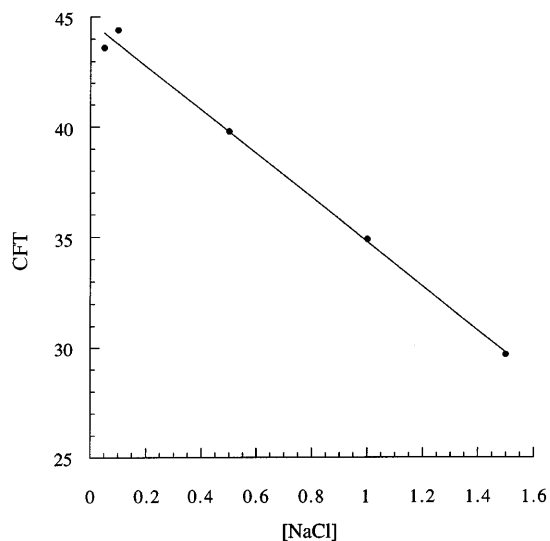


Fig. 7 CFT of poly[NIPMAM] latex 282 versus NaCl concentration

In Fig. 7, the CFT of the particles is plotted as a function of salt concentration (NaCl). As expected, a linear relationship between the CFT and the NaCl concentration is observed in the flocculation domain. The extrapolation of the curve to zero ionic strength gives a value of 44 °C, corresponding to the LCST of linear poly[NIPMAM] in pure water.

Generally, electrostatic repulsion is sensitive to added electrolytes, instead of a change in solvency as in the case of steric stabilization. In the case of poly[NIPMAM]

latexes, surface sulfate groups are responsible for electrostatic stabilization whereas the hydrophilic polymer chains of the shell layer of the particles provide a steric stabilization contribution. In addition, steric stabilization of such microgel particles is principally related to both the temperature and the salinity of the medium.

According to the relationship between the salinity and the LCST for thermosensitive linear polymers, it is difficult to distinguish between the colloidal aggregation induced by screening charged groups on the latex particles and the effect of solvency on poly[NIPMAM]. Therefore, the results reported on the colloidal stability (ccc) even at 20 °C do not exclude the effect of salt on particle shrinkage as already reported for core-shell poly(styrene/NIPAM) particles [27, 43].

Conclusion

The poly[NIPMAM] hydrogel latexes prepared as a function of polymerization temperature, initiator and cross-linker concentrations were characterized by examining the effect of temperature, pH and salinity on the colloidal properties.

- The particle diameter was found to decrease upon increasing the temperature, which confirms the thermal sensitivity of poly[NIPMAM] particles. In addition, a nonsharp decrease in particle size was observed when the temperature was close to the LCST of non-cross-linked linear poly[NIPMAM]. No significant effect of polymerization temperature and initiator concentration on the LCST was observed and the average LCST was found to be around 43 °C. In contrast, for the latexes prepared with various cross-linker (MBA) concentrations, the LCST obtained was dramatically dependent on the MBA concentration.

Therefore, for highly cross-linked particles, the transition domain was larger compared to slightly cross-linked particles.

- The measured electrophoretic mobility was found to be negative (in the pH domain of 3 to 11) irrespective of temperature. The negative electrophoretic mobility reflects the negative surface charge density originating from initiator decomposition. Moreover, the measured mobility was found to increase upon increasing the temperature as already observed for poly[NIPMAM] particles, which indicates the thermal sensitivity of poly[NIPMAM] latexes.
- The colloidal stability was investigated at room temperature. ccc values are higher than 1.5 M NaCl, showing that the particles are principally sterically stabilized below the transition temperature. To some extent, the colloidal stability of thermosensitive latexes cannot be discussed as for hard colloids (polystyrene, for example). In fact, salinity affects the solvency of poly[NIPMAM] in water, and consequently the LCST. In any case, the ccc determined at room temperature are higher compared to those obtained for colloids presenting only electrostatic stability, reflecting the steric stabilization of such particles. In addition, the steric stability was also evidenced by investigating the effect of temperature on the flocculation of particles (CFT experiments) at a given ionic strength.

Further studies are required to address the morphology of these microgel particles as a function of cross-linker agent (MBA) using an appropriate technique such as NMR by studying the magnetic relaxation of protons. In addition, more work is currently being developed for the preparation of poly(NIPMAM) microgel particles bearing reactive groups for the immobilization of biomolecules.

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