Effect of a cross-linking agent on the synthesis and colloidal properties of poly(*N*-isopropylmethacrylamide) microgel latexes

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SUMMARY: Microgel latex particles were prepared by batch precipitation polymerization of N-isopropylmethacrylamide (NIPMAM) monomer, using methylenebisacrylamide (MBA) and potassium persulfate (KPS) as a cross-linker and initiator respectively. Polymerization kinetics and final particle size as measured by quasi-elastic light scattering (QELS) at 20°C was not affected upon varying the cross-linker concentration. In contrast, the final particle size determined using both QELS (at 50°C) and SEM exhibits an increased in particle diameter upon increasing the MBA concentration. In addition, the amount of water soluble polymer was found to be directly related to the amount of MBA. Finally, the electrophoretic mobility behavior of the obtained latexes were investigated as a function of temperature.

Introduction

The preparation of hydrophilic stimuli-responsive microgel particles has attracted considerable attention over the past decade. In fact, stimuli-responsive microgels have been used in the biomedical field as solid phase supports to immobilize biomolecules and as drug delivery systems(1,2). Such microgel particles have been synthesized via precipitation polymerization as pioneered by Pelton et al.(3) using N-isopropylacrylamide (NIPAM) as a principal monomer and MBA as a cross-linker. If the polymerization studies of poly(alkyl(meth)acrylamide) hydrogel particles have already been reported,(4-6) only a few works(7,8) have been devoted to the effect of the cross-linker agent on the polymerization kinetics and colloidal properties of these microgel particles. The aim of this work was to investigate the effect of the cross-linker agent (MBA) on the polymerization process of NIPMAM (total conversion, particle size and morphology from SEM versus polymerization time, water soluble polymers formation) and on the colloidal characteristics of the final microgel particles (particle size as a function of temperature, LCST, swelling, electrokinetic and colloidal properties).

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Experimental section

Preparation of poly(NIPMAM) latexes

Poly(NIPMAM) latexes were prepared using batch precipitation polymerization of NIPMAM, (1g) as the principal monomer, MBA (from 0.02 to 0.2 g) as a cross-linker and KPS (2%w/w) as an anionic initiator. The polymerizations were conducted at 70°C with a constant stirring rate (200 rpm) and nitrogen stream. Polymerizations were performed in a 50 ml reactor for 6 hours. Details of synthesis (polymerization kinetic) and colloidal characterization have been reported in previous papers[5,9)]. The obtained latexes were first purified by repetitive centrifugation using deionized water and the water soluble polymer was removed and quantified.

Characterization of latexes

Lower Critical Solubility Temperature (LCST). The LCST temperature for each latex was determined by measuring the turbidity (i.e. optical density) variation as a function of temperature in a very highly diluted concentration (pH 6 and 10^{-5} M NaCl) at 500 nm wavelength using a Uvikon 930 Spectrophotometer. The temperature was controlled using an external thermostated water bath and the heating rate was 0.2 °C/min.

Particle size and distribution. Particles were first viewed by scanning electron microscopy (SEM) (Hitachi S 800) and the particle size in totally dehydrated state was measured. In addition, the hydrodynamic particle size was measured in 10^{-3} M NaCl using QELS (N4MD from Coulter)

Electrophoretic mobility. The electrophoretic mobility of all latexes was investigated at a constant pH=6.0 and in 10^{-3} M NaCl using the Zeta Sizer III, from Malvern Instruments.

Results and discussion

Particle size analysis

Particle size (at 20°C) versus polymerization time for various MBA concentrations reported in Figure 1 shows two domains : (i) the initial slope for a period of time less than 50 min shows that MBA seems to have no significant effect on the polymerization kinetics of NIPMAM during the particle growth step and (ii) the plateau exhibits micron-sized particles after 50 min of polymerization with no large difference in diameter considering the experimental error in this size range.

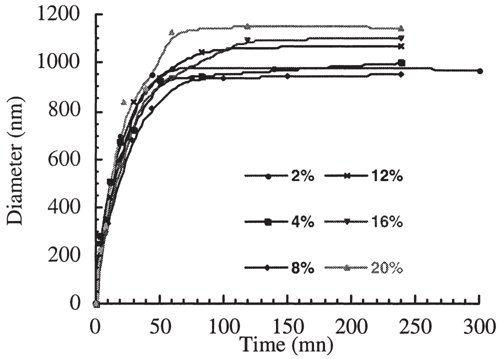

Figure 1 : Influence of MBA concentration on particle size measured at 20°C as a function of polymerization time.

Scanning electron microscopy (SEM) photographs, given in Figure 2, show that all latexes are highly monodisperse irrespective of the MBA concentration in the investigated range (from 2 to 16% w/w), except for 20% in which some associated particles are observed. The measured particle diameters are reported in Table 1.

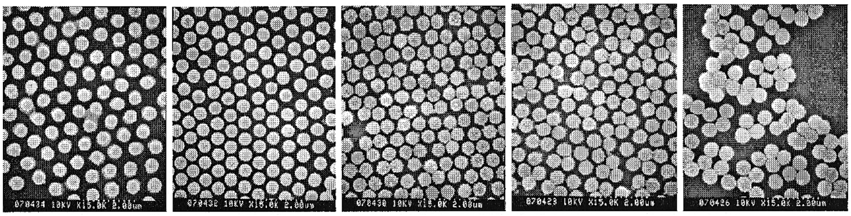

Figure 2 : Scanning electron micrographs (SEM) of all prepared latexes as a function of MBA concentration. (respectively 4, 8, 12, 16, 20% of MBA)

The final particle size determined using both by QELS at 50°C and SEM exhibits an increased in particle diameter upon increasing the MBA concentration. The ratio$(D_{20°C}/D_{50°C})^3$ determined using QELS measurement provides a qualitative estimation of the swelling capacity of the particles versus MBA concentration. In fact, it proves that the increase in MBA concentration leads to a decrease in the swelling factor, suggesting that the increasing connectivity of the polymer network has an influence on the swelling capacity of the microgel particles by the introduction of physical constraints. Similar behavior has already been observed by Wu et al[10)] by studying the swelling ability of poly(NIPAM) latexes versus MBA concentrations.

Table 1 : Particle size measured by QELS (at 20°C and 50°C) and by SEM as a function of MBA concentration used in the polymerization

MBA%	Diameter (nm) at 20°C	Diameter (nm) at 50°C	Diameter (nm) by SEM	Swelling factor $(D_{20°}/D_{50°})^3$
2	1030	446	400	12.3
4	1005	492	460	8.5
8	894	570	490	3.9
12	900	580	510	3.7
16	933	556	540	4.7
20	1120	613	570	6.1

Water soluble polymer formation

The influence of the cross-linker on the amount of water soluble polymer (WSP) produced during polymerization is reported in Figure 3. The WSP was found to decrease on increasing the MBA concentration in the polymerization recipe. This drastic phenomenon might be attributed to the cross-linking effect of MBA on the adsorbed water soluble polymer chains onto formed latex particles during the polymerization process. The role of MBA is indeed to prevent the poly(NIPAM) chains forming the latexes from dissolving when the particles are cooled below the LCST after polymerization time. It is therefore logical to obtain a decrease in WSP formation when increasing the amount of cross-linker agent in the polymerization.

Lower Critical Solubility Temperature (LCST)

The LCST of poly(NIPMAM) particles was determined for all latexes by measuring the optical density versus temperature. It was first observed that the LCST was not affected by the particle concentration. Figures 4 show the effect of 4 latex concentration after normalization respectively (raw data not shown), as evidenced, normalization allows to release from latex concentration.

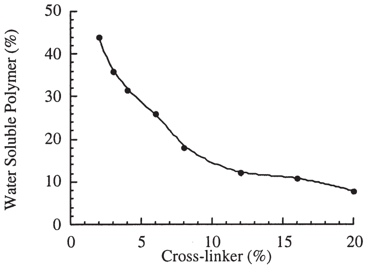

Figure 3: Influence of MBA concentration on the formation of water soluble polymer

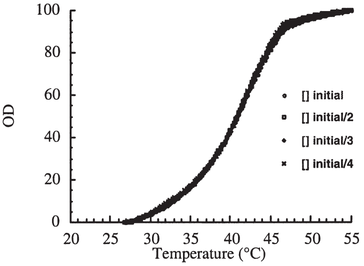

Figure 4: Normalized optical density versus temperature for four latex concentrations.

The normalized optical density as a function of temperature reported in Figure 5 shows the effect of MBA on the particles structure since the curve profile (OD vs. T) and the LCST domain depend on the latex composition (i.e. MBA concentration).

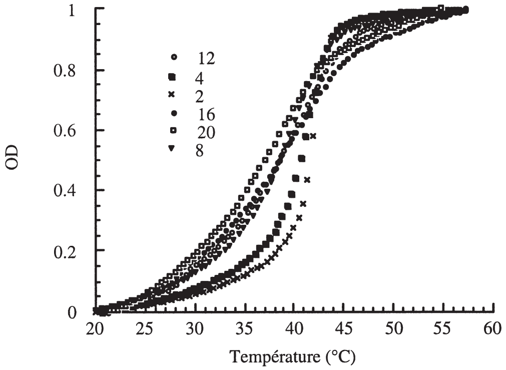

Figure 5 : Normalized optical density versus temperature for all latexes.

The transition range (i.e. LCST domain) can be explained by the structural inhomogeneities induced by the distribution of both the crosslinking density and charges within the particles. Concerning the cross-linker, the difference in reactivity between NIPMAM and MBA may cause heterogeneous distribution of the crosslinker in the polymer network, leading to higher connectivity in the centre of the particle than in the periphery. This observation explains the broad transition range observed in the case of cross-linked particles compared to free polymer (sharp transition).

If it is assumed that the LCST corresponds to the inflection point of OD curves versus temperature as established for linear thermosensitive polymers, the determined LCST's are found to be composition dependent as illustrated in Figure 6.

Electrokinetic study

The electrophoretic mobility of the prepared latexes was investigated as a function of temperature (Figure 7). Electrophoretic mobility was found to increase as the temperature was increased as first reported by Pelton et al[11)] in the case of poly(NIPAM) latexes. A drastic increase in electrophoretic mobility is clearly shown in the LCST range, which can be attributed to the shrinkage in particle size, leading to an increase of the surface charge density (SO_4^- groups coming from the initiator). The measured electrophoretic mobility vs. temperature for all prepared latexes exhibits the same curvature profile irrespective of MBA concentration. No clear trend can be conclued from this data.

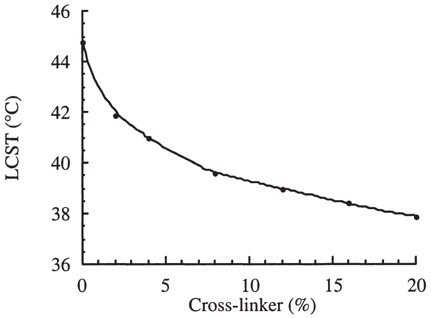

Figure 6: LCST as a function of MBA concentration.

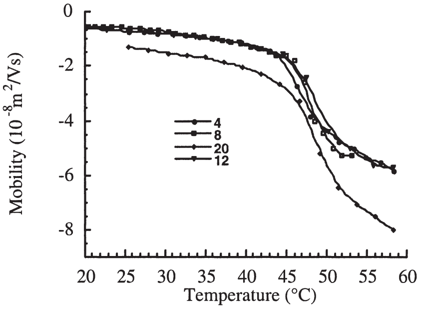

Figure 7: Electrophoretic mobility of poly(NIPMAM) latexes as a function of temperature (at pH 6 and 10^{-3} M NaCl).

Conclusion

Poly(NIPMAM) latexes as obtained by batch precipitation polymerization of NIPMAM, MBA exhibited narrow size distributed particles in MBA concentration ranging from 2 to 16%. The particle diameters measured at 50°C using QELS and SEM were found to increase with an increasing MBA concentration, whereas, the water soluble polymers recovered were drastically reduced. The optical density vs. temperature of all latexes showed that the LCST was significantly MBA dependent, since the transition took place in a much broader temperature range compared to the uncross-linked poly(NIPMAM). Electrophoretic mobility of latexes is increased upon raising the temperature above the LCST, due to a dramatic increase in the surface charge density; however one can not discriminate the influence of MBA concentration. This work clearly demonstrates that the introduction of topological constraints (MBA) results in a modification of the swelling capacity of the microgel network and modifies the thermodynamic parameters that determine the transition temperature (LCST).

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