

Kinetic Analysis of Poly(*N*-isopropylacrylamide-*co*-dimethylaminoethyl methacrylate) Microgel Latex Formation

Y. Zhang,^{1,2} L. S. Zha,^{1,3} S. K. Fu¹

¹Department of Macromolecular Science of Fudan University, The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Shanghai, China

²Modern Experiment Technology Center, Anhui University, Hefei, China

³College of Material Science and Engineering, Donghua University, Shanghai, China

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ABSTRACT: Curves of the conversion and particle size versus the time in the preparation of poly(*N*-isopropylacrylamide-*co*-dimethylaminoethyl methacrylate) microgel latices by surfactant-free emulsion polymerization were measured. The copolymerization reactions were rapid, and their rates increased with the dimethylaminoethyl methacrylate (DMAEMA) concentration in the polymerization recipe. Particle formation occurred by a homogeneous nucleation mechanism, in which DMAEMA helped to colloidal stabilize the primary particles. In addition, a strong dependence of the water-soluble-polymer (WSP) formation on the DMAEMA concentration was found, and the DMAEMA

content in the WSP was significantly higher than that in the microgel particle. A drastic variation of the crosslinking density within the microgel particle during the polymerization process was found through a comparison of the particle size determined by quasi-elastic light scattering with that determined by transmission electron microscopy. Finally, on the basis of these results, the mechanism of particle formation in this polymerization process was examined. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 839–846, 2004

Key words: microgels; copolymerization; kinetics (polym.); surfactants; emulsion polymerization

INTRODUCTION

In the past decade, thermally responsive poly(*N*-isopropylacrylamide) (polyNIPAM) microgel latices have attracted increasing attention because of their excellent properties, which make them candidates for many applications.¹ A drastic change in the hydrophilic–hydrophobic character of the particles at a given temperature [the so-called volume-phase-transition temperature (VPTT)] results in a correspondingly large change in their colloidal properties (especially their particle size, electrophoretic mobility, and colloidal stability).^{2–4} Therefore, such microgel particles exhibit outstanding capabilities for the separation and immobilization of biologically active molecules.^{5,6}

Previous works on the synthesis of polyNIPAM microgel particles were focused on the emulsion polymerization of *N*-isopropylacrylamide (NIPAM) with methylene bisacrylamide (MBA) as a crosslinker, in

the presence of an added surfactant (conventional emulsion polymerization)^{2,7} or in the absence of an added surfactant [surfactant-free emulsion polymerization (SFEP)].^{8,9} Conventional emulsion polymerization enables the preparation of very small microgel particles (i.e., particle diameters of less than ca. 150 nm); however, a problem with this technique is the difficulty of completely removing residual surfactants. SFEP does not suffer from residual surfactant contamination but does suffer from the difficulty of preparing small microgels because there is not enough available charge to stabilize a high concentration of small particles. The copolymerization of NIPAM with an ionic monomer by SFEP is another way of solving this problem. Introducing ionic groups at particle surface should increase electrostatic stabilization and create adsorptive sites for the molecules with the opposite charge.

Acrylic acid and methacrylic acid have been used as anionic monomers, which confer a negative charge to polyNIPAM microgel particles.^{10,11} Cationic polyNIPAM microgels can be prepared with a cationic monomer, such as 2-aminoethylmethacrylate hydrochloride¹² or vinylbenzylisothiuronium.¹³ The size of the polyNIPAM microgel particle can be adjusted by the amount of the incorporated ionic monomer. This is limited by the requirement that the polymer cannot be soluble in water at the polymerization temperature.

Correspondence to: S. K. Fu (skfu@srcap.stc.sh.cn).

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The surfactant-free emulsion copolymerization kinetics of a main monomer (e.g., styrene) with an ionic monomer have been widely investigated, and many studies have been focused on the effect of the type and concentration of the ionic monomer on the polymerization kinetics and mechanism.¹⁴ The ionic monomer plays a critical role in the polymerization mechanism in heterogeneous media, especially during the nucleation period and consequently on the final particle properties.¹⁵ In the case of the NIPAM copolymerization system, the water solubility of all monomers (NIPAM, MBA, and ionic monomer) and the thermosensitivity of the polymer are characteristic features of the surfactant-free emulsion copolymerization. The fundamental requirement for the formation of ionic poly-NIPAM microgel latex is that the polymerization in water be conducted above the cloud-point temperature (CPT) of the polyNIPAM copolymer. Under these conditions, water-soluble NIPAM copolymerizes with other monomers (e.g., MBA and ionic monomer) to give an insoluble copolymer, and the formed microgel latex particles are electrostatically stabilized above the CPT and principally sterically stabilized below the CPT. The ionic monomer copolymerization mechanism with NIPAM is expected to be different from that with styrene.

Dimethylaminoethyl methacrylate (DMAEMA) is a water-soluble monomer and contains tertiary amine groups that can be protonized in acidic solutions. Recently, we prepared monodisperse cationic thermosensitive latex microgels by the surfactant-free emulsion copolymerization of NIPAM, MBA, and DMAEMA (used as a cationic monomer).¹⁶ Adding the cationic monomer drastically reduced the particle size. The VPTT was found to be around 32°C and was slightly dependent on the concentration of the cationic monomer. The VPTT range became broader as the cationic monomer concentration increased.

The objective of this article is to analyze the kinetics of preparing poly(NIPAM-co-DMAEMA) microgel latices in the absence of a surfactant through the measurement of the NIPAM conversion and particle size versus the reaction time. Special attention is paid to the water-soluble polymer (WSP) produced during the growth of the particle. The concentration of DMAEMA is found to play an important role in the copolymerization kinetics and particle nucleation.

EXPERIMENTAL

Materials

NIPAM (Kasei Kogyo, Tokyo, Japan) and MBA (Fluka) were purified from 60/40 hexane/toluene mixtures and methanol, respectively. 2,2'-Azobis(amidinopropane)dihydrochloride (V50; Aldrich) was recrystallized from a 50/50 acetone/water mix-

TABLE I
Recipes for the Preparation of Poly(NIPAM-co-DMAEMA) Microgel Latices

Sample	NIPAM (mmol)	DMAEMA (mmol)
MG-1	48.34	0.16
MG-2	48.18	0.32
MG-3	47.86	0.64

The concentrations of the crosslinker MBA and the initiator V50 were kept constant for all of the recipes (MBA = 12 mmol/L, and V50 = 1.2 mmol/L). Total volume = 250 mL.

DMAEMA (Kasei Kogyo) was purified by passage through an alkaline Al₂O₃ column. HCl was reagent-grade and was used as received. Water was deionized before use.

Preparation

The polymerizations were conducted in a 250-mL, round-bottom, four-necked flask equipped with a poly(tetrafluoroethylene) (PTFE) anchor-shaped stirrer, a condenser, a thermometer, and a nitrogen inlet and outlet. The pH value of an aqueous solution of NIPAM (Kasei Kogyo, Tokyo, Japan), MBA (Fluka, Ronkonkoma, NY), and DMAEMA (Kasei, Kogyo) was adjusted to 4 through the addition of 0.1N HCl (in this case, DMAEMA was in its hydrochloride salt form, i.e., DMAEMAH⁺Cl⁻; for convenience, the simple nomenclature of DMAEMA is used in the following discussion). The solution was stirred at 200 rpm for 30 min with a nitrogen purge for the removal of oxygen, and the temperature was raised to 70°C with an oil bath with a thermostat. V50, dissolved in water, was added, and this marked the beginning of the polymerization reaction; an inert atmosphere was maintained throughout the experiment. One or two minutes later, opalescence appeared, and the reaction was continued up to 4 h. Detailed recipes are given in Table I.

Measurements

The samples taken during the reaction for kinetic measurements were quenched with traces of hydroquinone and stored at 4°C. The NIPAM (Kasei Kogyo, Tokyo, Japan) conversion was measured by gas chromatography (16A, Shimadzu, Japan). The column phase was 10% Carbowax 20 M (stationary phase, polyethylene glycol, MW 20,000; Scientific Instrument Services, New Jersey) on Chromosorb W (support, flux-calcinated, Aldrich, Milwaukee, WI), and detection was performed with a flame ionization detector (oven temperature = 200°C, detector and injector temperature = 250°C). The analysis method is described in detail in the literature.¹²

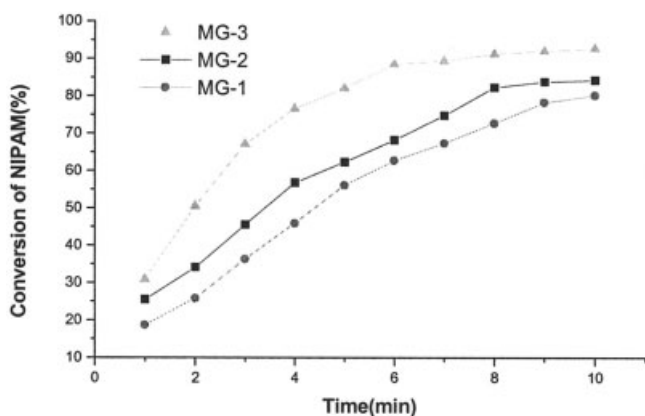


Figure 1 NIPAM conversion versus the reaction time as a function of the DMAEMA concentration in the feed recipe.

All the microgel particles were cleaned via repetitive centrifugation and redispersion cycles with deionized water. The supernatant collected from the first separation step was analyzed to determine the amount, composition, and CPT of the WSP.

Quasi-elastic light scattering (QELS; Autosizer 4700, Malvern, UK) and transmission electron microscopy (TEM; H-600, Hitachi, Japan) were used to investigate the water-swollen and collapsed particle size evolution, respectively, during polymerization. The amount of WSP was determined by a gravimetric method. The DMAEMA unit contents in the WSP and microgel particles were estimated by $^1\text{H-NMR}$ (DMX500, Bruker, Switzerland) with D_2O as the solvent. The CPT of the WSP was determined through the measurement of the optical density variation versus the temperature at 520 nm with a Kontron Uvikon 930 spectrophotometer (Milan, Italy).

RESULTS AND DISCUSSION

Conversion of the NIPAM monomer versus the polymerization time

The conversion of NIPAM was followed against the reaction time, as shown in Figure 1, which shows various curves for three different DMAEMA concentrations. In all cases, whatever the DMAEMA concentration was, the NIPAM conversion exceeded 80% within 10 min. This can be explained by the high propagation rate constant of the acrylamide derivatives associated with the heterogeneous character of the polymerization mechanism. Moreover, increasing the DMAEMA concentration clearly led to a steeper initial polymerization rate. This phenomenon can be attributed to the drastic effect of the DMAEMA concentration on the rate of the formation of the precursors, providing a large number of polymerization loci by a homogeneous nucleation mechanism.

Particle size versus the polymerization time

The influence of DMAEMA on the particle size versus the polymerization time was examined and illustrated in Figure 2, which shows the particle size by QELS at 25°C versus the time. The particle size rapidly leveled off within a few minutes; this reflected the short nucleation period leading to the formation of a constant particle number early in the polymerization process. The results obtained were in good agreement with those reported by Duracher et al.¹⁷ Figure 2 also shows that the particle size was DMAEMA-concentration-dependent. In fact, the final particle size decreased as the DMAEMA concentration increased in the polymerization recipe. This behavior was attributed to the fact that DMAEMA served to help to colloiddally stabilize the primary particles.

To obtain complementary insight into the surfactant-free copolymerization mechanism of NIPAM and DMAEMA, we analyzed latex particles by TEM at different reaction times. TEM photographs, such as those for MG-1 (Fig. 3) showed that highly monodisperse microgel particles formed as the polymerization proceeded, even at a low conversion (ca. 25%). This further corroborated a short nucleation step during the synthesis without a second nucleation.

Swelling ratio versus the NIPAM conversion

Figure 4 compares the particle diameters of the poly-(NIPAM-co-DMAEMA) microgel versus the NIPAM conversion determined by either TEM or QELS at 25°C, confirming that the size increased as the reaction proceeded. Nevertheless, the size measured by QELS at 25°C increased more rapidly than that obtained by TEM, and this reflected the swelling capacity of these thermosensitive particles in aqueous media below the VPTT. Indeed, the size measured by QELS at 25°C was

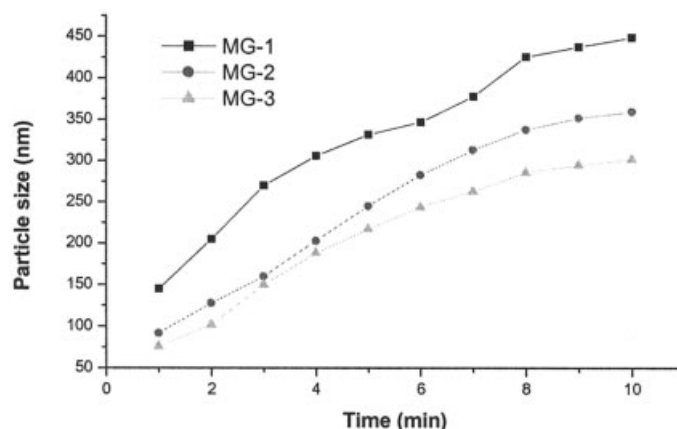


Figure 2 Effect of the DMAEMA concentration on the latex particle size (according to QELS at 25°C) as a function of time.

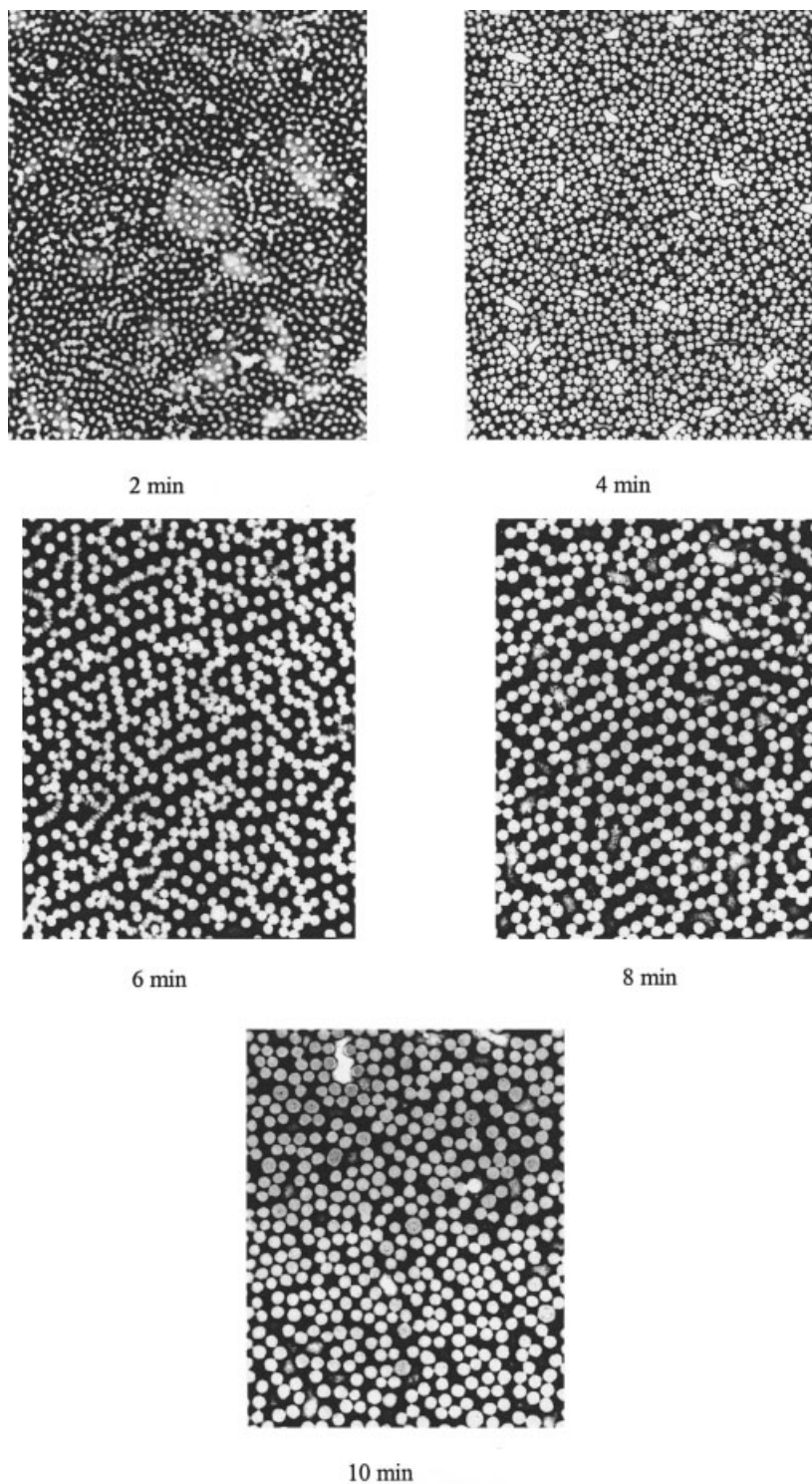


Figure 3 TEM images of MG-1 at various reaction times (original magnification = $1 \times 10^4\times$).

that of water-swollen particles (hydrodynamic diameter), whereas the size determined by TEM corresponded to particles in a dried state.

Swelling measurements have been traditionally used to characterize the crosslinking density of gels. In this work, we defined the swelling ratio as the ratio of the particle volume determined by QELS at 25°C to

that by TEM. At 25°C, the particle volume of poly(NI-PAM-co-DMAEMA) in water was sensitive to the amount of the crosslinker (MBA), whereas by TEM, the particle size was measured *in vacuo*, without water in the particles, and the particle volume should not have been very sensitive to small changes in the concentration of MBA in the particles. Therefore, the

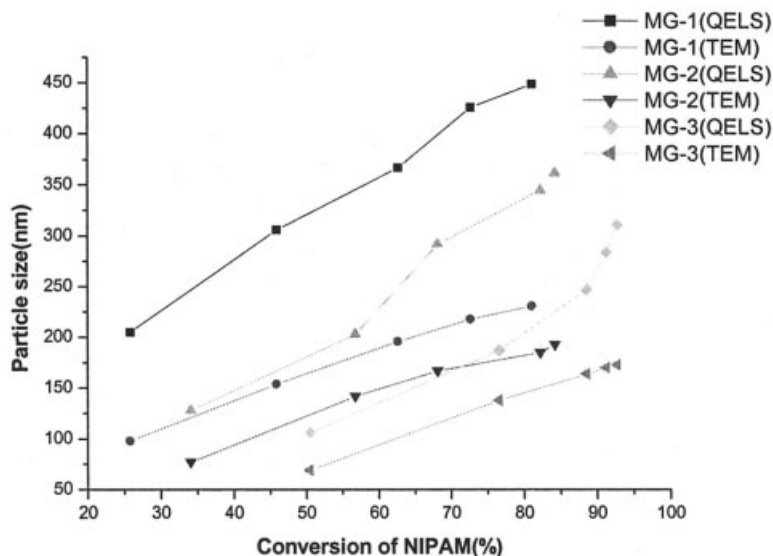


Figure 4 Effect of the DMAEMA concentration on the latex particle size according to QELS (25°C) or TEM as a function of the NIPAM conversion.

swelling ratio was a reliable estimate of the absolute degree of swelling at 25°C. The development of crosslinking within a microgel particle during the course of polymerization is illustrated in Figure 5, which shows that the swelling ratio decreased initially and then increased with conversion. The changes in the swelling ratio shown in Figure 5 are large; for example, for MG-2, the swelling ratio at an 84% conversion was 2.3 times greater than the value at a 57% conversion. The obvious explanation is that the earlier polymer that formed was rich in MBA, and this limited swelling; the latter polymer, formed within a particle, was much less crosslinked. Wu et al.⁷ mea-

sured the efficiency of MBA incorporation into the growing polyNIPAM microgel particles and found that the majority of the crosslinks were incorporated during the initial growth stage. This suggests that these particles contained a higher crosslinking density toward the center than at the periphery.

Another interesting feature of Figure 5 is that increasing the DMAEMA concentration led to a decrease in the swelling ratio. Because MBA, which was responsible for the polymer crosslinking density in the particles, was kept constant in the various experiments, the swelling behavior could be attributed to the variation of MBA in the particles. Presumably, two

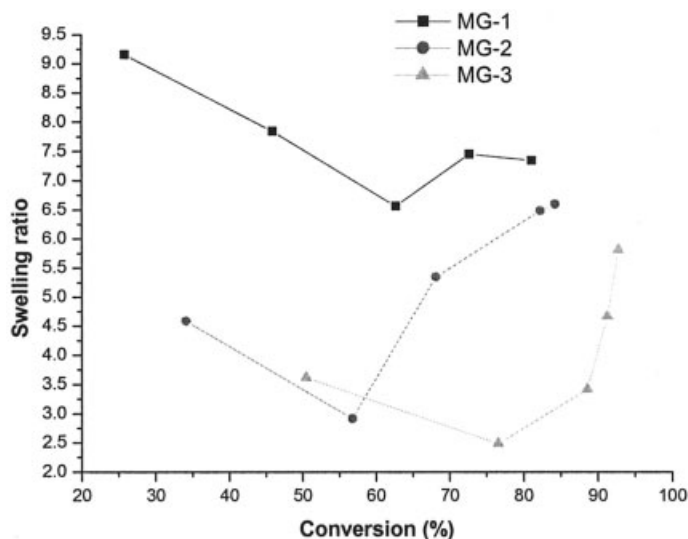


Figure 5 Effect of the DMAEMA concentration on the poly(NIPAM-co-DMAEMA) microgel swelling ratio as a function of the NIPAM conversion.

TABLE II
WSP Amount and DMAEMA Content in WSP and Microgel Particles

Sample ^a	WSP amount (wt %) ^b	Theoretical DMAEMA content (wt %) ^c	DMAEMA content in WSP by ¹ H-NMR (wt %)	Calculated DMAEMA content in the particle (wt %) ^d	DMAEMA content in the particle by ¹ H-NMR (wt %)
WSP-1	6.9	0.42	1.22	0.36	0.99
WSP-2	11.2	0.84	1.62	0.74	1.24
WSP-3	17.4	1.68	3.39	1.31	2.86

^a WSP-1, WSP-2, and WSP-3 correspond to the water-soluble polymers within the samples of MG-1, MG-2, and MG-3, respectively.

^b Determined by the gravimetric method.

^c From the feed recipe.

^d Calculated by the subtraction of DMAEMA amount in WSP from its total amount in the feed recipe.

effects of the DMAEMA concentration on the swelling ratio should be taken into account:

1. As the amount of DMAEMA increased in the polymerization recipe, it may be postulated that the MBA incorporation in the forming particles could be modified through a copolymerization effect, a change in the monomer partitioning, or both. DMAEMA incorporation improved the crosslinking distribution inside the microgel network and then influenced its swelling ratio.
2. The increase in the amount of the recovered WSP (see the following discussion), which was mainly composed of NIPAM and DMAEMA, led to an increase in the relative content of MBA inside the microgel network when the DMAEMA proportion was increased in the monomer mixture, and the crosslinking increase might also be attributed to the reduction of the swelling ratio.

WSPs

We analyzed the WSP produced during the formation of the microgels to clarify the polymerization kinetic of the cationic polyNIPAM microgels. Because the microgel particles could be separated from the latex serum upon centrifugation, it was feasible to determine the amount and nature of the water-soluble species recovered at the end of the polymerization, as reported in Table II. A marked increase in the amount of WSP was observed as the amount of DMAEMA increased in the recipe. This result might have originated in three ways: (1) the more rapid consumption of MBA, due to its reactivity being higher than that of NIPAM,⁷ resulted in more linear polymers, which exhibited less probability of being tightly crosslinked in the growing particles, especially at the end of polymerization; (2) some NIPAM copolymers with high DMAEMA contents held the CPT above the reaction temperature and would not precipitate in the aqueous medium; and (3) DMAEMA induced some transfer

reaction producing some low-molecular-weight chains with a low capacity for precipitation. We found that, when a high concentration of DMAEMA (>2.5 mol % with respect to the overall monomer concentration) was used, only the WSP was formed (no microgel latices). This was an indication that highly water-soluble DMAEMA could play a preponderant role in the process of nucleation and growth of the cationic microgel particles.

The CPTs for the recovered WSPs were measured, and the results are shown in Figure 6. The WSPs exhibited higher CPTs ($\geq 36^\circ\text{C}$) than free polyNIPAM in aqueous solutions (CPT $\sim 32^\circ\text{C}$). The difference in the CPT in the case of the WSPs could be attributed to the presence of electrical charges originating from the ionic monomer, which affected the transition of interfacial chains (a coil-to-globule transition).¹⁸ The cloud point of the WSP with a higher DMAEMA content was difficult to observe below 60°C because the copolymer was electrolytic in character and had little temperature sensitivity.

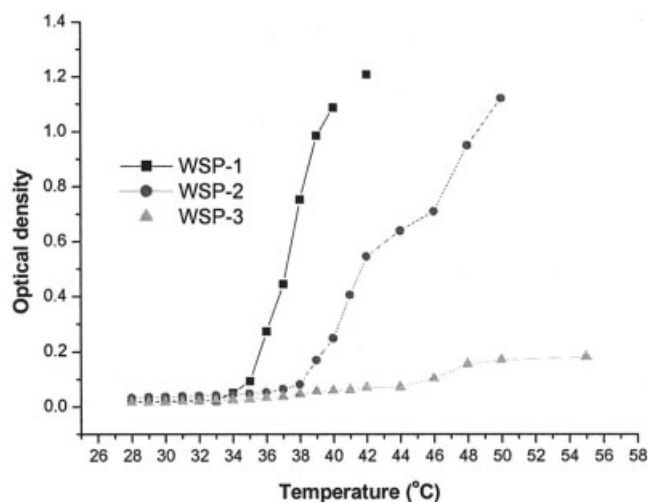


Figure 6 Variation of the optical density as a function of the temperature for different WSPs.

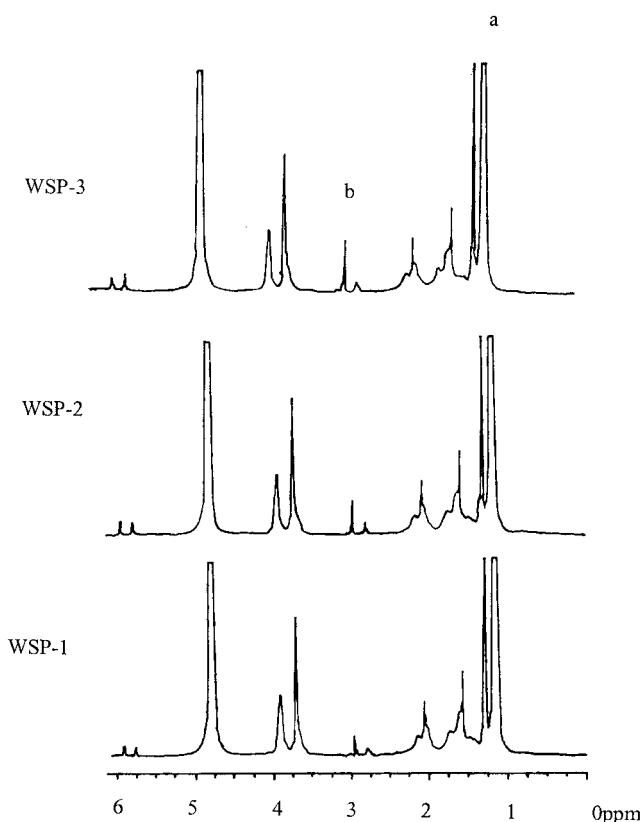


Figure 7 $^1\text{H-NMR}$ spectra of different WSPs.

To access the material balance of the cationic monomer (DMAEMA) in the WSP and microgel particles, we tried to establish a methodology that consisted first of quantifying the amount of WSP by a gravimetric method and subsequently analyzing the DMAEMA content by $^1\text{H-NMR}$ and second of calculating the DMAEMA content in the microgel particles by subtracting the amount of DMAEMA in the WSP from its total amount in the feed recipe. As shown in Figure 7, in addition to monomer and initiator traces, this recovered material (WSP) mostly contained the NIPAM/DMAEMA copolymer, and the characteristic peaks corresponding to the methyl groups in the NIPAM unit and DMAEMA unit were observed in the $^1\text{H-NMR}$ spectra at 1.17 and 2.95 ppm, respectively. A very small peak at 2.95 ppm, corresponding to the methyl group in the DMAEMA unit, was detected even at a concentration of 0.331 mol % DMAEMA to NIPAM in the polymerization recipe (sample MG-1). In addition, the DMAEMA unit contents in each WSP or microgel particle were obtained according to their respective peak area, as reported in Table II. The reported data reflect the fact that the DMAEMA contents in all WSPs increased, but the calculated contents of DMAEMA incorporated onto or into the particles decreased according to a comparison with their respective theoretical values. This suggested that the

NIPAM copolymer with a high DMAEMA content was hydrophilic and was difficult to precipitate to form primary particles. A direct analysis of the DMAEMA content in the particles dispersed in D_2O solutions by $^1\text{H-NMR}$ seemed feasible, as reported in Table II, and the detected contents were superior to their respective calculated values. This suggested that the poly(NIPAM-*co*-DMAEMA) chains were mainly located in the expanded shell layer of the latex particle.

Polymerization mechanism

On the basis of the previously reported kinetic results, we can outline qualitatively the mechanism of the surfactant-free emulsion copolymerization of NIPAM, MBA, and DMAEMA (used as a cationic monomer). Because of the nature of this polymerization system, the particle nucleation and growth of the cationic polyNIPAM microgel latices are separately described.

First, because the reaction temperature was well above the CPT of the NIPAM/DMAEMA copolymer, the precursors were formed only through the collapse of the oligomers produced in the aqueous phase according to the homogeneous nucleation mechanism. We have no precise data on the critical chain length (j_{crit}) for precipitation in the case of poly(NIPAM-*co*-DMAEMA), but it may be assumed that j_{crit} would increase with increasing DMAEMA concentration in the feed recipe. From TEM analysis and Figure 1, it seems that mature particles were formed at a very early stage, and this reflected the fact that the homo-coagulation step of the precursors spanned a very short time. The influence of the DMAEMA concentration on the particle size evolution versus the time could be interpreted by the occurrence of the suggested homogeneous nucleation mechanism. Increasing the DMAEMA concentration resulted in the formation of more precursors and contributed to the colloidal stability of the precursors.

Second, nucleated particles rapidly became the main polymerization loci, and their growth proceeded either by the capture of oligoradicals and subsequent propagation with monomers partitioned in the dispersed phase or by heterocoagulation of unstable precursors. The observation of highly monodisperse latices, even at intermediate conversions, would confirm such a growth mechanism and preclude any secondary nucleation step, regardless of the concentration of DMAEMA. Because of the relatively high reactivity of MBA in radical-initiated polymerization in comparison with NIPAM, the early collapsed chains were actually more crosslinked than those formed later. Moreover, the polymer chains created at the end of the reaction were loosely incorporated; therefore, they could be more easily disentangled and released upon cooling, providing the recovered WSPs.

CONCLUSIONS

1. Poly(NIPAM-*co*-DMAEMA) microgel polymerizations in water were rapid, and high conversions (>80%) were obtained within 10 min. The polymerization rates were raised as the DMAEMA concentration increased in the polymerization recipe.
2. Microgel particle formation occurred through homogeneous nucleation. DMAEMA incorporated into the microgels served to help to colloiddally stabilize the primary particles.
3. The WSP formation was strongly dependent on the DMAEMA concentration, and the DMAEMA content in the WSP was significantly higher than that in the microgel particle. The poly(NIPAM-*co*-DMAEMA) chains were mainly located in the expanded shell layer of the latex particle.
4. There was evidence of significant variations of the crosslinking density within the microgel particles during the course of the polymerization.

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