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Preparation of Poly(N-isopropylacrylamide) Microgels using Different Initiators Under Various pH Values

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Ammonium persulfate (APS), 2,2′-azobis(amidinopropane) dihydrochloride (V50) and 4,4′-azobis(4-cyanovaleric acid) (ACVA) were utilized to prepare temperature-sensitive poly(N-isopropylacrylamide) (PNIPAM) microgels by precipitation polymerization under various reaction pH conditions. Their particle sizes and swelling ratios depended on the reaction pH due to the pH dependence on the ionization degree of the decomposed fragments originating from the initiators and their hydrophilicity-hydrophobicity. The more hydrophobic initiator, under the reaction pH conditions used, could be partitioned to a greater extent into the microgel particles due to the hydrophobicity of PNIPAM chains at the reaction temperature, which led to a more cross-linked structure inside the microgels resulting in their smaller swelling ratio. pH dependence of surface charge density of the microgels with amidino groups or carboxylic acid groups on their surfaces was evidenced by the variation of their zeta potentials as a function of pH.

Keywords temperature-sensitive microgels, poly(N-isopropylacrylamide), ammonium persulfate, 2,2′-azobis(amidinopropane) dihydrochloride, 4,4′-azobis (4-cyanovaleric acid), pH dependence

Introduction

In the past decade, increasing attention has been focused on both the preparation and characterization of temperature-sensitive microgels. Much published work has dealt with both fundamental aspects and practical applications of such microgels, mostly with poly(N-alkyl(meth)acrylamide) derivatives such as poly(N-isopropylacrylamide) (PNIPAM) (1–3), poly(N-isopropylmethacrylamide) (PNIPMAM) (4) and poly(N-ethylmethacrylamide) (PNEMAM) (5). A drastic change in the hydrophilic-hydrophobic character of these microgels at a given temperature [the so-called volume phase transition temperature (VPTT)] results in a correspondingly large change in their colloidal properties, such as their particle size, surface charge density and colloidal stability (6). As a

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consequence, many applications were developed to take advantage of such properties, especially in the biological field (7).

The temperature-sensitive microgels based on alkyl(meth)acrylamide as monomer were prepared through a radical-initiated precipitation polymerization process in the aqueous phase. N,N′-methylene bisacrylamide (MBA) was mostly used as crosslinker, and potassium persulfate (KPS) (or ammonium persulfate (APS)) and 2,2′-azobis(amidinopropane) dihydrochloride (V50) were usually used as initiator. The effect of reaction temperature and crosslinker agent on the polymerization process (polymerization kinetics, conversion, final particle size, morphology, water-soluble polymer etc.) have primarily been presented and discussed (4, 5, 8, 9), while there have been few reports on the influence of the initiator on the precipitation polymerization. As expected, the initiator plays an important role in the polymerization process, especially during the nucleation period, and consequently, on the final microgel properties. The role of the initiator in the formation of PNIPAM microgels can be considered as follows: (1) initiating the polymerization of the monomer and the crosslinker in the water phase leads to the formation of oligomers, which are precipitated to produce precursor particles when their critical chain lengths are reached or when the crosslinked chains start to precipitate; (2) the charged groups resulting from the decomposed fragments of the initiator on the surfaces of PNIPAM microgels electrostatically stabilize these colloidal particles.

In this work, APS, V50 or 4,4′-azobis(4-cyanovaleric acid) (ACVA) were used to initiate the precipitation polymerization of NIPAM (N-isopropylacrylamide) and MBA to form temperature-sensitive microgels. Because the hydrophilic nature of V50 and ACVA is dependent on the degree of dissociation of the carboxylic acid groups and protonation of the amidino groups, respectively, the influence of reaction pH value on the particle sizes, swelling ratios and zeta potentials of PNIPAM microgels was investigated. pH dependence of surface charge density of the microgels with amidino groups or carboxylic acid groups on their surfaces was evidenced by the variation of their zeta potentials as a function of pH.

Experimental

Materials

NIPAM (Acros) and MBA (Aldrich) were purified by repetitive recrystallization in 60/40 pentane/toluene mixture and methanol, respectively. APS (Shanghai Shoushi Chemical Co.), V50 and ACVA (Acros) were used as received. Water was deionized before use by a Millipore apparatus (Direct-Q).

Preparation and Purification of Microgel Latexes

The polymerization experiments were performed using a batch polymerization process. The pH of 48 ml aqueous solutions of 1 g NIPAM and 0.1 g MBA was adjusted to a certain value by adding 0.1 N HCl or 0.1 N NaOH solution. After the solution was stirred for 30 min with a nitrogen purge to remove oxygen, its temperature was raised to 70°C. 0.05 mmol initiator (APS, V50 or ACVA) dissolved in water of corresponding pH was added into the reaction solution, which marked the beginning of the polymerization reaction, and a nitrogen atmosphere was maintained throughout the experiment. One or two minutes later, opalescence appeared, and the reaction was continued for

4 h. All microgel particles were cleaned via repetitive centrifugation and redispersion cycles using deionized water.

Characterization

The hydrodynamic diameter (DH) of the PNIPAM microgel particles at 20°C and 50°C were determined by quasi-elastic light scattering (QELS) (Malvern, Zetasizer Nano-ZS), and their swelling ratios were calculated as $(D_H(25°C)/D_H(50°C))^3$. The temperature sensitivity of the microgel particles was investigated by measuring the absorbency of a highly diluted microgel dispersion as a function of temperature (ranging from 20°C to 50°C) with an ultraviolet spectrophotometer (Perkin-Elmer, Lambda 35) at 500 nm. The heating rate was 0.1 K min^{-1} and was kept constant. The zeta potentials of the microgel particles were measured with a Zetasizer Nano-ZS as a function of pH at 20°C or 50°C. All values were obtained by taking the average of at least three measurements.

Results and Discussion

The Effect of pH Value of Reaction Medium on the Particle Size and the Swelling Ratio of PNIPAM Microgels

APS, V50 and ACVA are three different initiators, being an inorganic salt, organic base and organic acid, respectively. APS is soluble in both acidic and basic aqueous solutions, but V50 is soluble in acidic or neutral solutions and ACVA is only soluble in basic solutions. In the precipitation polymerization process for preparing PNIPAM microgels, an upper pH limit for V50 was 7.0 and a lower pH limit for ACVA was 9.0, while the pH range for APS was from 2 to 12, otherwise the latexes were found to be partially or totally flocculated beyond the pH limit or the pH range. This shows that the pH of the polymerization medium had an effect on the nucleation step and the microgel stability.

The effect of reaction pH value on the particle size of PNIPAM microgels based on APS, V50 or ACVA as initiator was examined keeping constant the mole concentration of initiators, as shown in Table 1. The increase in reaction pH value decreased the particle size of PNIPAM microgels based on APS or ACVA as initiator, but increased the one based on V50 as initiator. This is due to the fact that the dissociation degree of the sulphate acid groups or carboxylic acid groups resulting from the decomposed fragments of APS or ACVA, respectively, increased with the increase of the pH, while the protonation degree of amidino groups derived from the decomposed fragments of V50 decreased with the increase of the pH. More charged groups enhanced the formation of more precursor particles and increased the colloidal stabilization of the nucleated particles through an electrostatic mechanism, thus lowering the final particle size of PNIPAM microgels. This argument can be further evidenced by the variation of the zeta potentials of the PNIPAM microgel latexes against the reaction pH value, as exhibited in Table 2.

The particle size measured by QELS at 20°C was that of water-swollen PNIPAM microgel, whereas the size at 50°C corresponded to the microgel in a collapsed state. We defined the swelling ratio as the ratio of the particle volume determined by QELS at 20°C to that at 50°C. The swelling ratio could be used to evaluate the crosslinking density of the PNIPAM microgel. The effect of reaction pH value on the swelling ratios of PNIPAM microgels based on APS, V50 or ACVA as initiator was examined, as shown in the last column of Table 1. Under constant concentration of the crosslinker

Table 1
Particle sizes and swelling ratios of PNIPAM microgels prepared using different initiators under various pH conditions[a]

Samples	Initiators	pH values of reaction medium	Particle sizes (nm) 25°C	Particle sizes (nm) 50°C	Swelling ratios
APS-3	APS	3.0	703	452	3.75
APS-5	APS	5.0	670	395	4.85
APS-8	APS	8.0	647	375	5.13
V50-3	V50	3.0	635	386	4.42
V50-5	V50	5.0	673	406	4.56
V50-7	V50	7.0	743	516	2.98
ACVA-9	ACVA	9.0	640	416	3.62
ACVA-10	ACVA	10.0	544	343	3.98
ACVA-11	ACVA	11.0	518	315	4.42

[a]Measured at pH 6.

(MBA) used in the polymerization recipe, increasing the reaction pH value led to a decreases in the swelling ratio of the PNIPAM microgels based on V50 as initiator, but an increase for the PNIPAM microgels based on APS or ACVA as initiator. The decrease in swelling ratio was attributed to a more cross-linked structure of the microgels, which may be formed by the decomposition and crosslinking reaction of the initiator partitioned into the microgel particles. Because the hydrophobic nature of the initiators can be adjusted by changing the pH, therefore, the more hydrophobic the initiator at the reaction pH, the more the amount of the initiator partitioned into the microgel particles due to the hydrophobicity of PNIPAM chains at the reaction temperature.

Table 2
Zeta potentials of PNIPAM microgels using different initiators under various reaction pH conditions[a]

Samples	Initiators	pH value of reaction medium	Zeta potentials (mv) 25°C	Zeta potentials (mv) 50°C
APS-3	APS	3.0	−4.4	−46.1
APS-5	APS	5.0	−6.4	−49.3
APS-8	APS	8.0	−8.5	−48.7
V50-3	V50	3.0	11.9	37.5
V50-5	V50	5.0	8.9	34.3
V50-7	V50	7.0	2.9	24.9
ACVA-9	ACVA	9.0	−2.9	−23.6
ACVA-10	ACVA	10.0	−6.5	−30.8
ACVA-11	ACVA	11.0	−8.3	−35.5

[a]Measured at pH 6.

The Effect of Initiator Species on the Volume Phase Transition Temperature (VPTT) of PNIPAM Microgels

The VPTTs of all PNIPAM microgels, determined by measuring the absorbency of a highly diluted dispersion as a function of temperature, corresponds to the inflexion points of the absorbency variation versus temperature curves, as illustrated in Figure 1. It can be pointed out that there is no significant effect of the initiator species on the VPTT value. This could be explained by the phenomena that the content of decomposed fragments of initiators in the microgel particles was very low, and they were mostly located on the surface of the particles.

The Effect of pH Value of Dispersion Medium on the Zeta Potentials of PNIPAM Microgels

The surface charge density of the temperature sensitive microgels with ionizable groups resulting from the initiators used in the polymerization recipe can be determined by zeta potentiometry. The investigation of zeta potentials versus pH can be considered as a key point for the analysis of surface charge density variation. Since amidino groups and carboxylic acid groups are weakly basic groups and weakly acidic groups, respectively, their degree of ionization should rely on the pH value of the media. The surface charge density of the microgels with amidino groups or carboxylic acid groups on their surfaces depends on the pH value of the media. Because the surface charge density of colloidal particles is proportional to their zeta potential, we measured the zeta potential variation of PNIPAM microgel latexes against the pH value of the media at temperatures both below (20°C) and above (50°C) their VPTT to evaluate the effect of pH on their surface charge density, as shown in Figure 2. The PNIPAM microgels based on V50 as the initiator in the polymerization recipe had positive zeta potentials due to the protonation

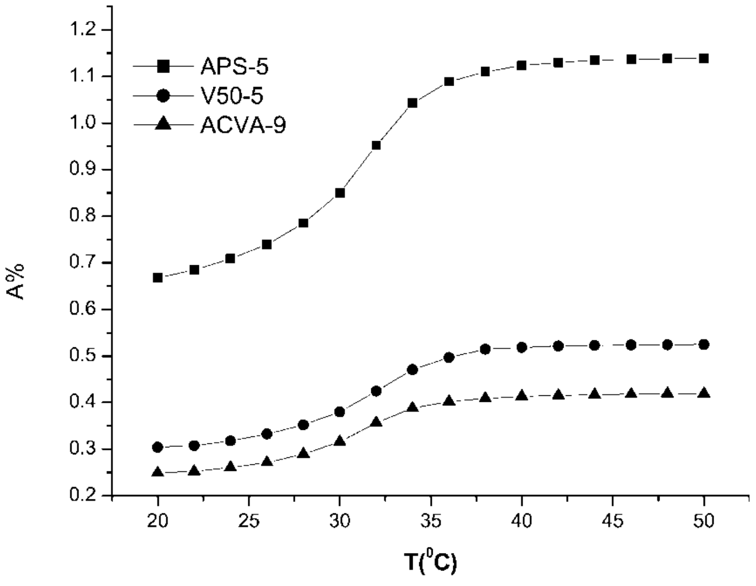

Figure 1. The curve of the absorbency variation of highly diluted PNIPAM microgel dispersion vs. temperature (pH = 6).

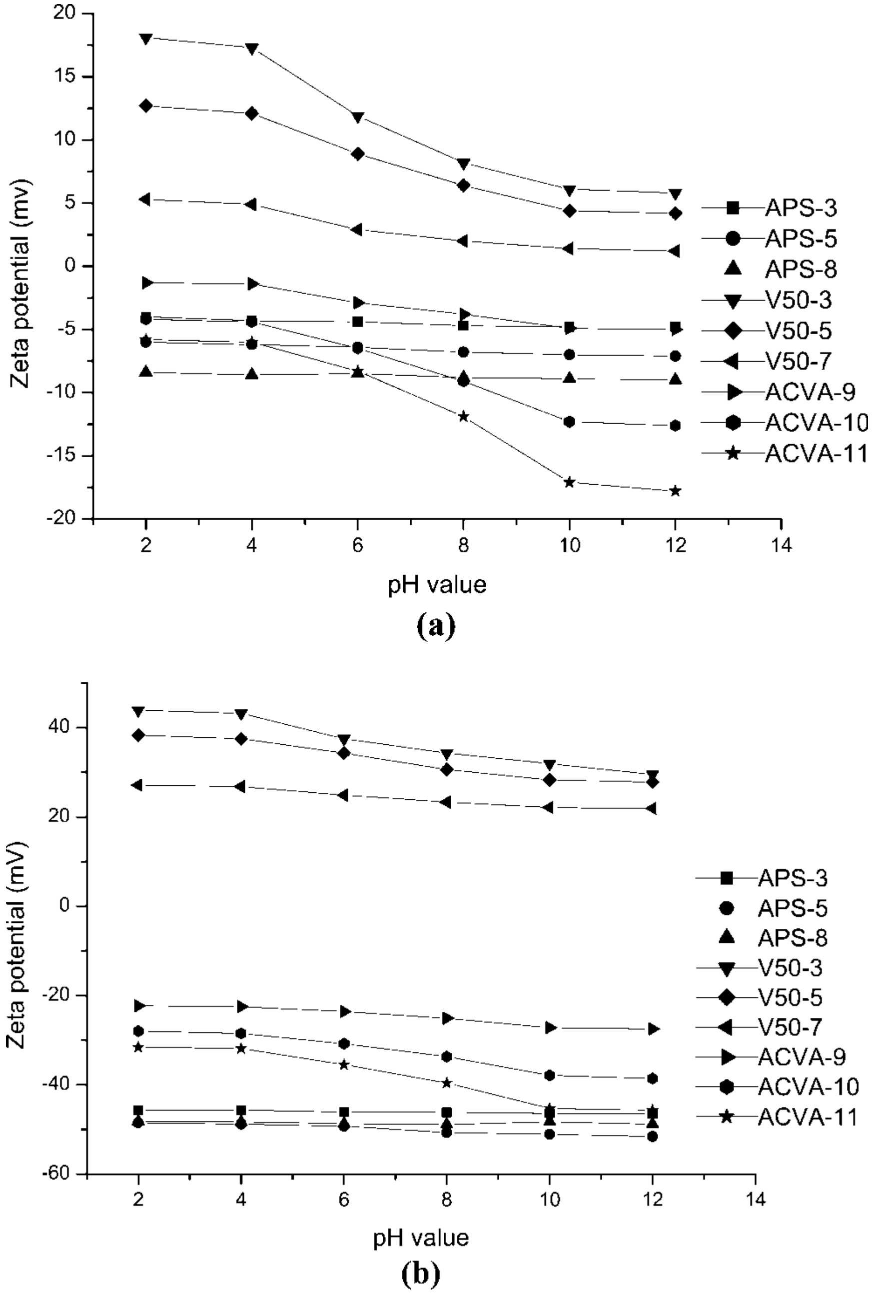

Figure 2. Variation of the zeta potentials of PNIPAM microgels against pH value at 25°C (a) and 50°C (b).

of amidino groups originating from V50 on their surfaces, and they decreased markedly as the medium pH values increased from 4 to 10, reflecting the lowering of the degree of protonation of the amidino groups. Comparatively, the PNIPAM microgels based on ACVA as the initiator have negative zeta potentials due to the dissociation of the carboxylic acid groups deriving from ACVA on their surfaces, and the absolute value of their zeta potentials was raised significantly as the medium pH value increased from 4 to 10, representing the enhancement of the dissociation of the carboxylic acid groups. Because the sulphate group is a strong acid group, the zeta potentials of the PNIPAM microgels based on APS as the initiator are slightly dependent on the medium pH value. Comparing Figure 2(a) and (b), the measured absolute values of zeta potentials as a function of pH above the VPTT were found to be higher than that below the VPTT for all the PNIPAM microgels, irrespective of the nature of the surface charge. This observed behavior can be explained by an increase in the surface charge density induced by the reduction in particle size due to the temperature-sensitivity of these microgels.

Conclusions

Three different initiators, ammonium persulfate (APS), 2,2′-azobis(amidinopropane) dihydrochloride (V50) and 4,4′-azobis(4-cyanovaleric acid) (ACVA), were used to prepare temperature-sensitive PNIPAM microgels by precipitation polymerization. Their particle sizes and swelling ratios were dependent on the reaction pH due to the pH dependence of the ionizing degree of their decomposed fragments and their hydrophilicity-hydrophobicity. The microgels with amidino groups or carboxylic acid groups based on V50 or ACVA as initiator, respectively, have sharp pH dependence of surface charge density.

Acknowledgements

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