STABILITY OF POLY(*N*,*N*′-METHYLENEBISACRYLAMIDE-*co*-4-VINYLPYRIDINE) MICROGEL DISPERSION AND ADJUSTMENT OF THE HYDROPHOBICITY IN THE MICROGELS[*]

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Abstract In the UV-Vis spectra of pure light-scattering systems, there is an exponential relationship between absorbance and wavelength ($A = K\lambda^{-n}$). Here, the exponent *n* is named as flocculation-coagulation parameter. In the present paper, the effects of different additives on the stability of poly(*N*,*N*′-methylenebisacrylamide-*co*-4-vinylpyridine) (poly(Bis-*co*-4-VP)) microgel dispersion were studied in detail via this parameter. The results showed that the stability of the dispersion mainly comes from the ionization of pyridine groups, making the microgel positively charged on its surface. This was confirmed by the measurement of Zeta potential and the result of conductometric titration. The result of fluorescence analysis indicated that the hydrophobicity in the microgels is enhanced with the increase in total 4-VP unit content.

Keywords: Microgel dispersion(s); 4-Vinylpyridine; Flocculation-coagulation parameter; Zeta potential.

INTRODUCTION

The methods of dispersion and conventional emulsion polymerization are usually used for the preparation of microgels[1, 2]. In these methods, the presence of surfactants and stabilizers can prevent the microgel particles from aggregation and plays an important role in stabilizing the dispersions[3]. Since the surfactants and stabilizers cannot be completely removed from the microgels, they can affect the nature of the polymers, confining the application of the microgels to some fields. So surfactant-free emulsion polymerization has been widely used in recent years[4, 5]. The presence of electrostatic repulsion derived from the decomposition of ionic initiator and steric barrier contributes to the stability of the dispersions[6, 7]. In this method, the solid content of the dispersions is limited because gels are always generated at monomer contents higher than 2.5%[6], also confining the application of the dispersions.

On the condition that the dose rate was 25.1 Gy/min and the total dose was 1 kGy, a stable microgel dispersion, with solid content of about 3.4% and average hydrodynamic radius ($\overline{R}_h$) of 56.2 nm, was successfully obtained from the dilute solution of 4-vinylpyridine (4-VP, 0.04 mol/L) and *N*,*N*′-methylenebisacrylamide (Bis, 0.2 mol/L) by surfactant-free emulsion polymerization using γ-ray irradiation[8]. Unlike those initiated by ionic initiators, this copolymerization initiated by γ-ray irradiation cannot cause electrostatic repulsion, so it is necessary to study the stability conditions in order to increase the solid content of the dispersion produced by surfactant-free emulsion polymerization, to control the state of the copolymer and to put the microgel into practice.

The copolymers of 4-VP with Bis and other crosslinking agents exhibit their characteristics in adsorption of organic molecules[9] and in the field of catalysis[10]. Since these characteristics are closely related to the

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hydrophobicity in the copolymers, it is important to study the effect of the total 4-VP unit content on the hydrophobicity in the microgels for the application purpose.

EXPERIMENTAL

Materials

Bis (Beijing Chemical Reagents Company, analytical grade) was purified by recrystallization and dried under vacuum. 4-VP (Merck, > 96%) was purified by vacuum distillation. Ethyl 2-(4-aminophenyl)-3,3-dimethyl-3H-indole-5-carboxylate, as shown in Fig.1, was synthesized and purified according to the procedure described in the literature [11], and the detailed information about the compound has been reported in Ref. [11]. Potassium chloride (KCl), potassium sulfate (K_2SO_4), magnesium chloride ($MgCl_2$), hydrochloric acid (HCl), acetic acid (HAc), urea, L-phenylalanine (L-Phe), ammonia (NH_3) and other reagents (Beijing Chemical Reagents Company, analytical grade) were used as received. Water used in the experiments was deionized and redistilled.
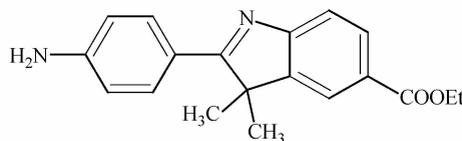
Ethyl 2-(4-aminophenyl)-3,3-dimethyl-3H-indole-5-carboxylate

Fig. 1 Chemical structure and name of the fluorescent probe molecule

Preparation of Microgels

The feed solutions contained desired amounts of Bis, 4-VP and water. After the monomers were dissolved completely, the feed solutions were transferred into test tubes (diameter: 15 mm) to a certain height, bubbled with high-purity N_2 for 20 min to remove O_2, then sealed and irradiated for a definite time at a special location in the ^{60}Co irradiation field whose dose rate was determined by Fricke dosimeter. The products were purified by dialysis against water. $\bar{R}_h$ values of all samples (56–152 nm) have been detected by dynamic light scattering and reported in Ref. [8] in detail. In all experiments except detecting the change of hydrophobicity in the microgels, the same sample with a feed ratio of [4-VP]:[Bis] = 1:5 was used, which is representative and has the best transmittance and the maximal solid content among all samples.

UV-Vis Spectra

Fixed amounts of purified microgel dispersion and a certain amount of additive (KCl, K_2SO_4, $MgCl_2$, HCl, HAc, L-Phe, urea or NH_3) were mixed, then water was added to keep the total volume constant. After sufficient mixing, UV-Vis spectra between 380 and 810 nm were recorded by using a U-3010 Spectrophotometer (Hitachi, Japan) with 1 cm quartz cells. Water was used as the reference in each case.

For pure light-scattering system, there exists the following empirical expression[12, 13]:

$$A = K\lambda^{-n} \tag{1}$$

or
$$\lg A = \lg K - n \lg \lambda \tag{2}$$

where A is absorbance, K is a constant related to the particle volume and refractive index of the particle and the solution, λ is the wavelength of light, and n is an exponent. If the particle size is smaller than $\lambda/10$ (Rayleigh scattering region), then the n value is 4. As the particle size increases, the n value decreases as a result of internal interference. In other words, n can be used to monitor the flocculation of the particles sensitively[12, 13]. Based on Eq. (2), the value of n can be obtained from the slope of the straight line. The experimental error was estimated to be about 2%–3%.

Figure 2 shows that the microgel does not exhibit its character absorption in the wavelength range from 380 to 800 nm within which the decrease in the light intensity of the dispersion results from the scattering of particles. It can also be seen that $\lg A$ has a good linear relationship with $\lg/\lambda$. Therefore, n can be used to monitor the flocculation of the microgel.
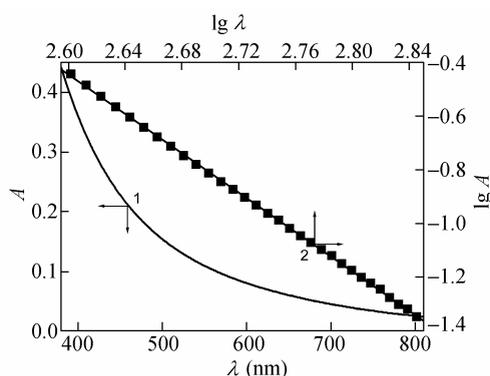
Fig. 2 Visible spectrum of the microgel (curve 1) and linear relationship between lg A and lg λ (curve 2)
Dose: 1 kGy; Dose Rate: 23.5 Gy/min; [4-VP]:[Bis] = 1:5; [4-VP] + [Bis] = 0.24 mol/L

Absorbance at 547 nm

Samples were prepared by following the preparation method of the UV samples mentioned above. After sufficient mixing, their absorbance (A_b) at 547 nm was measured with water as the reference in each case. After centrifugation (4000 r/min) for 30 min, the absorbance of the upper dispersion (A_a) was measured at the same wavelength. The difference between A_b and A_a is given as follows:

$$\Delta A = A_b - A_a \tag{3}$$

Thus, ΔA was used to monitor the coagulation of the microgel. The experimental error was estimated to be about 2%–3%.

Zeta Potential (ζ)

The ζ was measured by using a zeta potential analyzer (Brookhaven Instruments Corporation) at 25°C. The sample was prepared by diluting the microgel dispersion with KCl solution (0.01 mol/L).

Conductometric Titration

A definite amount of purified microgel dispersion was diluted by degassed water to a certain volume. After sufficient mixing, they were titrated by HCl solution through micrometer syringe and the conductivity was measured at (17.0 ± 0.1)°C by a DDS-307 Conductivity Meter (Shanghai, China) under N_2 atmosphere. From the conductometric titration curves, concentration and content of 4-VP unit on the surface of the microgels can be obtained. Provided that the pK_b of 4-VP unit in the microgel is close to that of 4-isopropylpyridine whose pK_b is 7.98[14] considering their structural similarity, the ionization degree of 4-VP unit and the content of ionized 4-VP unit on the surface of the microgels can be estimated.

Fluorescence Spectra

A definite amount of purified microgel dispersions and small amount of stock solution of fluorescent probe molecules in methanol were mixed, and the aqueous solution of sodium hydroxide (pH = 8.5) was added to keep the volume constant. Buffer solution was not used as described in Ref. [15]. After sufficient mixing, the fluorescence spectra were measured using an F-4500 Fluorescence Spectrometer (Hitachi, Japan). The excitation wavelength at 360 nm, with excitation and emission slit widths of 10 nm, was selected. The scanning speed was 1200 nm/min.

RESULTS AND DISCUSSION

Effects of Additives on the Stability of the Microgel Dispersion

Figure 3 shows that there are two inflexion points in the curve of ΔA versus [KCl]. One inflexion point appeared at a lower KCl concentration corresponds to the critical coagulation point of the microgel, while the other at a

higher KCl concentration — the complete coagulation point. These two concentrations are called the critical coagulation concentration and the complete coagulation concentration of KCl, respectively. There are also two inflexion points in the curve of n versus [KCl]. One inflexion point where the concentration of KCl is lower corresponds to the critical flocculation point of the microgel, and the KCl concentration is called the critical flocculation concentration of KCl. The other inflexion point also reflects the complete coagulation concentration and it is consistent with that obtained from the curve of ΔA versus [KCl]. It is obvious that the microgel dispersion is much more sensitive to electrolytes than the poly(N-isopropylacrylamide) (PNIPAM) latex, which was sterically stabilized at room temperature[6]. So it can be concluded that the stability of the microgel dispersion mainly comes from the electrostatic repulsion but not from steric barrier.
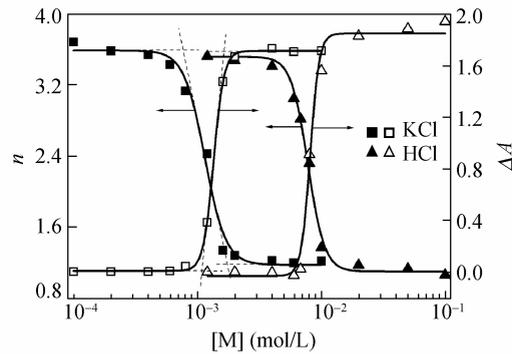
Fig. 3 Curves of ΔA versus [M] and n versus [M]
M represents different additives. The synthesis condition of the microgel is same as that mentioned in Fig. 2.
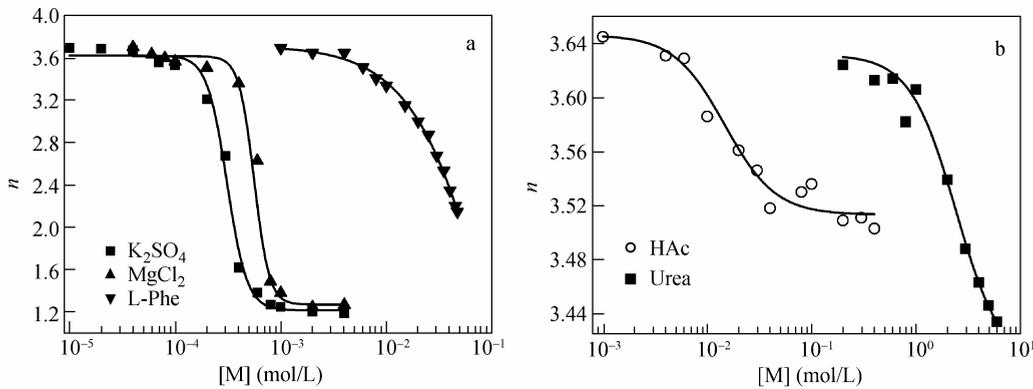
Fig. 4 Curves of n versus [M]
a) Non-acid strong electrolytes and amphoteric electrolyte; b) weak acid and non-electrolyte
M represents different additives. The synthesis condition of the microgel is the same as that mentioned in Fig. 2.

Similarly, for HCl, there are also two inflexion points in Fig. 3 and the complete coagulation concentrations obtained by the two methods are equivalent. Because n can be used to monitor not only the flocculation but also the coagulation, therefore, it is named the flocculation-coagulation parameter in this paper. The critical coagulation concentration can be affected by many factors and it is not so sensitive as the critical flocculation concentration. Thus, flocculation-coagulation parameter was used to evaluate the effect of additives on the stability of the microgel dispersion. K_2SO_4, $MgCl_2$, HAc, urea, L-Phe and NH_3 were also used to test the stability of the microgel dispersion besides KCl and HCl. All of the results are summarized in Figs. 4 and 5, and also compiled in Table 1.

Figure 4(a) and Table 1 show that the critical flocculation and complete coagulation concentrations of K_2SO_4 are the lowest among those of the selected additives, and those of $1/2MgCl_2$ and KCl are nearly identical.

It is clear that anions play a key role in the flocculation and coagulation of the dispersion, and the efficiency of the flocculation and coagulation increases with the increase in the valence of anions. Thus, it is believed that the microgel is electropositive. This is confirmed by the value of ζ of the microgel dispersion, which was measured to be (1.0 ± 0.2) mV, one order of magnitude lower than the absolute value of ζ of poly(*N*-isopropyl-acrylamide) (PNIPAM) latex measured by Saunders and co-workers[7]. The Hamaker constant of the microgel dispersion was calculated to be 4.3×10^{-20} J by the critical coagulation concentration (*ccc*) and the following formulas[7]:

$$\gamma = \frac{\exp(\frac{ze\psi_d}{2kT}) - 1}{\exp(\frac{ze\psi_d}{2kT}) + 1} \tag{4}$$

$$ccc = \frac{98500\varepsilon^3 k^5 T^5 \gamma^4}{N_A\, e^6 A_{eff}{}^2 z^6} \tag{5}$$

$$A_{eff}{}^{1/2} = A_p{}^{1/2} - A_w{}^{1/2} \tag{6}$$

where T is the absolute temperature, ψ_d is equal to the value of ζ of the microgel dispersion, A_{eff} is the effective Hamaker constant, A_p is the Hamaker constant for the microgel dispersion, A_w is the Hamaker constant for water $(3.7 \times 10^{-20}$ J), N_A is Avogadro constant, ε is the dielectric constant of solvent, k is Boltzmann constant, e and z have their usual meanings. After sufficient dialysis, there exist no other species besides weak basic pyridine group that can generate positive charge in the microgel. Therefore, it can be concluded that the positive charge comes from the ionization of pyridine groups introduced by 4-VP.

HCl and HAc can react with pyridine groups, increasing the positive charge of the microgel and making the dispersion more stable. Table 1 shows that the critical flocculation concentrations of HCl and HAc are much higher than those of KCl and 1/2 MgCl$_2$. HCl is a strong electrolyte, so it can make the microgel coagulate completely, while HAc is a weak electrolyte, which cannot act efficiently as HCl. Figure 4(b) shows that there also exists an inflexion point besides the critical flocculation point, which represents the appearance of a certain stable state, but not of the complete coagulation point because the mixture is still translucent and the corresponding value of flocculation-coagulation parameter is high (about 3.51).

Table 1. Critical flocculation, critical coagulation and complete coagulation concentrations of several additives (all the values are obtained from the corresponding intersection points of tangents in the curves of *n* or ΔA versus the concentration of additives)

	Standing time (h)	Flocculation-coagulation parameter		ΔA	
		Critical flocculation concentration (mol/L)	Complete coagulation concentration (mol/L)	Critical coagulation concentration (mol/L)	Complete coagulation concentration (mol/L)
K$_2$SO$_4$		2.01×10^{-4}	4.76×10^{-4}		
1/2 MgCl$_2$		7.89×10^{-4}	1.60×10^{-3}		
KCl		7.54×10^{-4}	1.70×10^{-3}	1.08×10^{-3}	1.70×10^{-3}
HCl		5.35×10^{-3}	1.08×10^{-2}	6.76×10^{-3}	1.08×10^{-2}
HAc		4.78×10^{-3}			
L-Phe		1.42×10^{-2}			
Urea		9.52×10^{-1}			
NH$_3$	3	6.97×10^{-3}	1.65×10^{-2}		
	24	2.58×10^{-3}	9.26×10^{-3}		
	72	1.34×10^{-3}	6.39×10^{-3}		

It is known that urea can denature proteins and influence the conformation of water-soluble polymers. Figure 4(b) shows that urea makes the microgel flocculate slightly and not coagulate in the selected concentration range, and its critical flocculation concentration is much higher than those of the other selected additives. This phenomenon may be ascribed to the hydrophobic interaction mechanism between urea and the microgel[15]. It can also be seen that hydrophilicity from both $-CONH-$ groups introduced by Bis and $-OH$ groups introduced by γ-ray irradiation initiation only plays a less important role in the stabilization of dispersion.

L-Phe is an amphoteric electrolyte with an isoelectric point at 5.48, so it can interact with pyridine groups to a certain extent. It is also noticed that the positive charge on the surface of the microgel turns the random orientation of L-Phe molecules in the bulk solution to the state of $-COO^-$ group closing to the microgel in the hydrated layer that is confined near the surface of the particle. The electric double layer that makes the dispersion stable is compressed and the stability of the dispersion declines. $-NH_3^+$ and $-COO^-$ groups enter the hydrated layer simultaneously because of the special amphoteric structure of L-Phe molecules. However, the electrostatic repulsion limits the L-Phe concentration in the hydrated layer. So flocculation appears only when L-Phe is concentrated and it cannot make the microgel coagulate completely in the selected concentration range (Fig. 4a). The critical flocculation point in this system is less apparent than that in other additive systems. This may be explained by the fact that the L-Phe concentration in the hydrated layer is lower than that in bulk solution. The above characteristics of L-Phe make it possible to adjust the state of the copolymer in a relatively wide concentration range.

The pK_b of NH_3 is 4.75 while that of 4-VP unit in the microgel should be close to 7.98 as mentioned above. It is obvious that the basicity of NH_3 is stronger than that of 4-VP unit and can inhibit the ionization of the latter. The result is that the quantity of the positive charge on the surface of the microgel is reduced and that the stability of the dispersion descends. This is the reason that NH_3 can make the microgel flocculate and coagulate (Fig. 5). Because both NH_3 and 4-VP units in the microgel are weak bases, the inhibition process is slow. Figure 5 illustrates that NH_3 has an obvious time effect on the flocculation and coagulation of microgel.
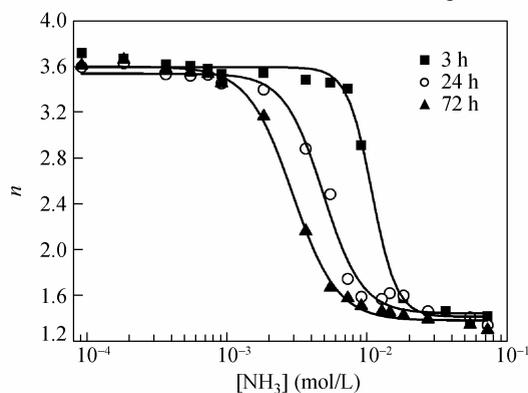
Fig. 5 Effect of the concentration of NH_3 on n at various times
The synthesis condition of the microgel is the same as that mentioned in Fig. 2.

Charge and 4-VP Unit Content on the Surface of the Microgel

At the end of copolymerization, the dispersion was analyzed by thin-layer chromatography on SiO_2 thin plates with ethyl acetate/petroleum ether (9/1, *V/V*) as eluent to detect the presence of any unreacted 4-VP, and none was found. This means that almost all of the 4-VP has taken part in the copolymerization.

Figure 6 shows the conductivity curve of the microgel dispersion obtained by titration with HCl, which is similar to that of weak bases titrated with strong acids, so the microgel dispersion is basic. It is shown in the curve, the amount of HCl corresponding to the inflexion is 6.15 μmol, which is much less than the 4-VP content in the microgel (200 μmol). So it is assumed that the inflexion point corresponds to the titration end-point of surface 4-VP unit. Because the positive charge comes from the ionization of pyridine groups introduced by 4-VP, the charge content on the surface of the microgel is estimated according to the hypothesis described above, and

the results are listed in Table 2. It can be seen that the charge content on the surface of the microgel is one order of magnitude less than that of electronegative PNIPAM microgel synthesized by Mcphee *et al.*[16], which is consistent with their difference in ζ. It is possible that the hydration ability of cations is much stronger than that of anions[17].
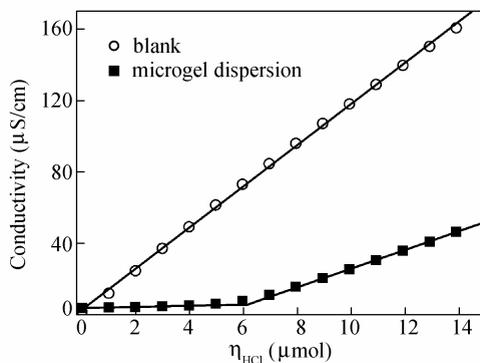
Fig. 6 Conductivity curve of microgel dispersion measured by titration with HCl Microgel dispersion: 5 mL, [HCl] = 0.01984 mol/L; The synthesis condition of the microgel is the same as that mentioned in Fig. 2.

Table 2. Charge and 4-VP unit content on the surface of the microgel

[4-VP]:[Bis]	Weight of polymer (g/5 mL microgel dispersion)	n_{HCl} (μmol/5 mL microgel dispersion)	Surface 4-VP unit content (μmol/g polymer)	Surface charge content (μmol/ g polymer)
1:5	0.1771	6.15	34.7	0.10
PNIPAM latex				3.79[16]

Hydrophobicity in the Microgels

In the past few years, we have focused our study on some substituted 3H-indoles in various molecular assemblies[15, 18–20]. It was found that substituted 3H-indoles were sensitive in detecting the change of the microenvironment. Here, ethyl 2-(4-aminophenyl)-3,3-dimethyl-3H-indole-5-carboxylate, as a member of the family of substituted 3H-indoles, was used to detect the change of the hydrophobicity in the microgels with various 4-VP unit contents. The 3H-indole molecules are not rigid and the phenyl ring can liberate within the *kT* energy barrier. This torsional movement is responsible for the geometric changes taking place in the ground and excited states and provides an important deactivation pathway for the S$_1$ state. According to the INDO/S semi-empirical calculations, this main nonradiative decay pathway has been ascribed to the formation of a nonemissive twisted intramolecular charge transfer (TICT) state originating in the amino group[21, 22]. In water, it is the formation of the TICT state that results in the fluorescent quenching, while in hydrophobic circumstance the TICT state is inhibited to a great extent and the fluorescence intensity (I_f) is enhanced[20]. Figure 7 shows that the I_f value of the probe molecule is enhanced when the 4-VP unit content in the microgels increases. In other words, the hydrophobicity in the microgels is enhanced with the increase of total 4-VP unit content. Since water is a non-solvent for the linear poly(4-vinylpyridine) (P4VP)[23], it can be concluded that the region containing P4VP segmers increases and that the hydrophobic environment is generated by the intertwist and the warp of these segmers. Thus, the hydrophobicity of the microgels can be adjusted by changing the ratio of 4-VP and Bis in the feed solution to satisfy the requirements.

At the present time, it is difficult to find any relationship between the stability of the microgel dispersion and the hydrophobicity in the microgels although both of them are of theoretical and practical importance.
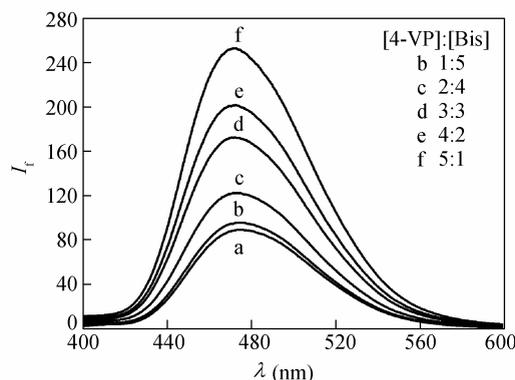
Fig. 7 Emission spectra of the fluorescent probe molecules in water (a) and in the microgel dispersions with various 4-VP unit contents (curves b–f) Dose: 3 kGy, Dose Rate: 23.5 Gy/min; [4-VP] + [Bis] = 0.24 mol/L

CONCLUSION

The stability of the dispersion mainly comes from the ionization of pyridine groups, making the microgel positively charged on its surface. This was confirmed by the measurement of Zeta potential and the result of conductometric titration. The result of fluorescence analysis indicates that the hydrophobicity in the microgels is enhanced with the increase in total 4-VP unit content.

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