

## pH and Organic Solvent-Sensitive Properties of Crosslinked Polymeric Spheres Formed by a Soap-Free Emulsion Polymerization

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**ABSTRACT:** Narrowly distributed poly (styrene-*co*-(4-vinylpyridine)) microspheres are facilely prepared by a soap-free emulsion polymerization, and their structures and properties are investigated by TEM, FTIR spectra, DSC, and DLS, respectively. The sizes and glass transition temperatures of the polymeric spheres increase with an increase of 4-vinylpyridine in the reactive system. In addition, these polymeric spheres show good stability in water and a series of organic solvents due to their crosslinked structures. When poly(styrene-*co*-(4-vinylpyridine)) microspheres are obtained in the reactive system where the weight ratio of 4-vinyl pyridine to styrene is less than 4/6, they can be well dispersed in water as well as in organic solvents such as ethanol, toluene and DMF, and show obvious pH sensitive and organic solvent-sensitive characteristics. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** copolymers; crosslinking; emulsion polymerization; colloids

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### INTRODUCTION

Micro-and/or nanopolymeric spheres have been extensively studied due to their unique structures and properties together with their wide applications in many fields.<sup>1–9</sup> In the past few decades, much effort has been directed towards controlling their sizes, constructing their structures and functions.<sup>10–12</sup> The typical research work includes the novel three-layered composite spheres with the core-shell-corona structure prepared by self-assembly of metallic nanoparticles and different block copolymers,<sup>10</sup> the carrier of palladium nanoparticles prepared by using polymeric spheres,<sup>11</sup> and the multilayer polymeric microspheres with different layer structures prepared by a step-by-step synthesis method.<sup>12</sup>

Among the mostly researched polymeric micro- and/or nanospheres, the environmental-sensitive ones have been specially focused on, because they can conventionally adjust their behaviors or functions according to external stimulus, such as pH,<sup>13</sup> temperature,<sup>14</sup> ionic strength,<sup>13</sup> light,<sup>15</sup> and magnetic field.<sup>16</sup> One of the mostly well-documented environmental-sensitive polymers is based on pH-responsive ones including methacrylic acid-based alkali-swallowable polymers,<sup>17</sup> *N*-isopropylacrylamide-based copolymers containing either acidic or basic comonomers,<sup>18</sup> acid-swallowable polymers based on basic monomers such as 4-vinylpyridine (4VP), 2-vinylpyridine(2VP), or tertiary amine methacrylates such as 2-(diethylamino) ethyl methacrylate (DEA), or 2-(diisopropylamino)- ethyl methacrylate (DPA).<sup>19</sup>

Because the polymeric spheres with pH-responsive characteristics are expected to produce novel materials with a superior structure and function, the particular attention about them have been attracted in recent years.

To successfully introduce the pH-responsive components into the polymeric spheres, various preparation methods have been developed. Emulsion polymerization is generally used to prepare polymeric spheres with the response characteristics. However, this method typically requires a large amount of emulsifier or cosurfactant which makes post-treatments more complicated.<sup>20</sup> Dispersion polymerization, performed in the presence of a second soluble polymer as a steric stabilizer, has also been carried out for preparing polymeric spheres.<sup>21</sup> Unavoidably, the steric stabilizer becomes attached to the surface of the precipitating polymers formed in the reaction, which causes the lack of reproducibility in dispersion polymerization since it is highly sensitive to a subtle change of parameters involved in the polymerization process. Recent years, self-assembly offers the key to build up polymeric spheres with favorable properties and therefore becomes greatly attractive. Our previous work demonstrated that polymeric spheres were prepared by means of the self-assembly method based on block copolymers.<sup>7,10</sup> The as-prepared spheres inherently having functional groups could not only exhibit colloidal stability due to electrostatic repulsion but also act as complex agents for further deposition of noble metal nanoparticles.<sup>7,10</sup> The drawbacks of this method generally include the noxious

**Table I.** The Preparing Recipes of the Polymeric Spheres and their Properties

Sample	St (g)	4VP (g)	DVB (g)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	H <sub>2</sub> O (mL)	Conversion (wt %)	$\bar{d}_n$ (nm)	C <sub>v</sub>	T <sub>g</sub> (°C)
csv-10	10.0	0	0.4	0.4	120	86.5	449	23.7	109.5
csv-82	8.0	2.0	0.4	0.4	120	85.4	340	21.3	116.6
csv-64	6.0	4.0	0.4	0.4	120	85.1	357	15.1	129.3
csv-46	4.0	6.0	0.4	0.4	120	84.9	479	6.4	140.6
csv-28	2.0	8.0	0.4	0.4	120	80.7	761	2.2	148.8

organic solvent used in preparing process, the low concentration of the polymeric spheres and the discommodious operations. Furthermore, the structure of the polymeric spheres is easily destructed in water or many other organic solvents, which greatly inhibits their applications in many fields.

The aim of the present work is to facily synthesize pH-sensitive and organic solvent sensitive polymeric spheres, which are stable not only in water but also in a series of organic solvents. With these aims, styrene, 4-vinyl pyridine are selected as comonomers and divinylbenzene is selected as a crosslinker, and the pH and organic solvent sensitive poly (styrene-co-(4-vinylpyridine)) spheres are synthesized by one-step in water and characterized by TEM, FTIR, and DSC. The selected poly (styrene-co-(4-vinylpyridine)) spheres are then dispersed in water and different organic solvents and their pH-sensitive as well as organic solvent-sensitive characteristics are investigated by DLS. Although the synthesis mechanism of the uncrosslinked poly (styrene-co-(4-vinylpyridine)) spheres have been shown before,<sup>22,23</sup> the less attention has been paid to the properties of the crosslinked polymeric spheres in water and different organic solvents, which are closely corresponded to their applications.

## EXPERIMENTAL SECTION

### Materials

Styrene (St, Acros Organics, 99%) and 4-vinylpyridine (4VP, Acros Organics, 95%) were purified by vacuum distillation prior to use. Water used in this study was purified with a Millipore Mill-Q system and the resistivity was above 16 MΩ cm<sup>-1</sup>. Divinylbenzene isomers (DVB,80%) was supplied as technical grade by Shengli Technical Factory, China, which was washed with 5% aqueous sodium hydroxide, water and then dried over anhydrous magnesium sulfate prior to use. The initiator potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, AR grade, was purchased from Tianjin Chemical Company) and all other reagents were used as received.

### Synthesis of pH and Organic Solvent Sensitive Crosslinked Poly(St-co-4VP) Spheres

The synthesis recipes of the polymeric spheres were seen in Table I. In a typical recipe, styrene (6.0 g), 4-vinylpyridine (4.0 g), DVB (0.4 g), water (120 mL) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.4 g) were added in a round bottom flask. The flask was deoxygenated by bubbling N<sub>2</sub> through the solution for 15 min. Then the flask was immersed into an oil bath at 70°C and polymerization allowed to proceed for 6 h at a strong stirring rate of 500 rpm using a magnetic stirrer. After completion of polymerization, products were centrifuged at 8000 rpm for 30 min, followed by careful

decantation of the supernatant water, replacement with fresh water, and redispersion of the sediment particles with the aid of an ultrasonic bath. This protocol was used to remove the residual monomers. Then the precipitate was filtered and dried in a vacuum oven at 60°C for 24 h. The sample was denoted as CSV-64, in which the CSV represents the crosslinked polymeric sphere with styrene and 4-vinylpyridine, the numbers of 6 and 4 represent 6.0 g styrene and 4.0 g 4-vinylpyridine. The other samples were denoted by the similar method.

### Characterization

The conversion was calculated from the weight percent of the dried precipitates to the monomer and crosslinker. The morphology of the polymeric sphere was observed by using a Philips T20ST transmission electron microscopy (TEM) at an acceleration voltage of 80 kV, whereby a small drop of polymeric sphere suspension was deposited onto a carbon-coated copper EM grid and dried at the same temperature at atmospheric pressure. The sizes and size distributions of the polymeric spheres were determined by TEM and all of the TEM size data reflected the averages about 20–100 particles each. The number-averaged diameter  $\bar{d}_n$  and the coefficient of variation of the polymeric sphere size distribution C<sub>v</sub>, were calculated according to the following formulae:

$$\bar{d}_n = \left( \frac{\sum n_i d_i}{\sum n_i} \right), \quad \delta = \left( \frac{\sum (d_i - \bar{d}_n)^2}{\sum n_i} \right)^{1/2},$$

$$c_v = \frac{\delta}{\bar{d}_n} \times 100$$

Here, the  $n_i$  in the equation is the number of the polymeric sphere with a diameter equal to  $d_i$ . The less the value of C<sub>v</sub> is, the more narrow the size distribution will be. Fourier transformation infrared spectra (FT-IR) were recorded at 25°C using a TENSOR 37 FT-IR spectrometer. All FT-IR spectra were obtained within the range of 4000–400 cm<sup>-1</sup>; 32 scans were collected at a resolution of 1 cm<sup>-1</sup>. The differential scanning calorimeter (DSC) was recorded with a Netzsch (Germany) DSC 204 at a heating rate of 10°C min<sup>-1</sup> under an N<sub>2</sub> atmosphere from 0 to 200°C. Dynamic laser scattering (DLS) measurements were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm at 25°C. All measurements were performed in 0.01 wt % dispersions that had been equilibrated for at least 20–40 min in water with the desired pH adjusted by adding either HCl or NaOH or in an organic solvent, and the measurements were done at an angle of 90°. The detailed method of DLS could be found elsewhere.<sup>24</sup>  $\zeta$  potentials were

calculated from the measured electrophoretic mobilities determined using the Malvern Nano ZS ZEN3600 instrument. Measurements were averaged over 20 runs using dilute dispersions (0.01 wt %) at different pH values. The measurements were carried out at 25°C. The structure stability of the poly (St-co-4VP) spheres was evaluated by observing the morphologies of the dried particles after being treated by an organic solvent or by calculating the weight ratio of the dried particles after and before being extracted with DMF. The morphologies of the particles are observed under TEM after a small drop of suspension in toluene or ethanol is deposited onto a carbon film-coated copper EM grid and dried. In the extracting experiment, polymeric spheres (3.0 g) were first wrapped by a filter paper and immersed in DMF (100 mL). The polymeric spheres were then extracted in the filter paper by DMF for 24 h. The structure stability of the poly (St-co-4VP) spheres was evaluated by the value of  $m/m_0$ . Here,  $m_0$  and  $m$  were the weight (g) of the dried poly (St-co-4VP) spheres before and after being extracted, respectively. The larger value of  $m/m_0$  indicates the better structure stability of the particles.

## RESULTS AND DISCUSSION

The pH and organic solvent sensitive poly (St-co-4VP) spheres with crosslinked structures are synthesized via a soap-free emulsion polymerization by utilizing  $K_2S_2O_8$  as an initiator, 4-vinylpyridine and styrene as monomers, and divinylbenzene as a crosslinker. The synthesis mechanism is that of the poly (St-co-4VP) sphere formation,<sup>22,23</sup> except that crosslinkers are added in the present case. In light of this mechanism, the soap-free emulsion polymerization system initially forms the oil phase of 4-vinylpyridine, styrene, and divinylbenzene and aqueous phase. Under a strong stirring condition, the interface of oil/aqueous phase is deformed and the oil phase is dispersed into two parts, i.e., oil droplets of monomers (monomer phase) and monomer molecules in aqueous phase. To lower the interfacial tension between droplets and water, the oil droplets tend to adsorb the hydrophilic  $S_2O_8^{2-}$  anions on their surfaces.<sup>25</sup> Meanwhile, the hydrophilic 4-vinylpyridine preferentially distributes on the surfaces of the oil droplets which are comprised of a hydrophilic component of 4-vinylpyridine and a hydrophobic one of styrene and divinylbenzene.<sup>25</sup> At the polymerization temperature, the reaction begins and the oligomer radicals form in the interface of oil/aqueous phase and aqueous phase. Because the concentration of 4-vinylpyridine in aqueous phase is much higher than that of styrene, and furthermore, the bulk copolymerization reactivity ratios of 4-vinylpyridine is higher than that of styrene, the formed oligomer radicals are dominated by 4-vinylpyridine.<sup>22,26</sup> The oligomers generated in the interface mainly acts as nucleus for the particle formation while the oligomers generated in aqueous phase mainly provide the surface-active molecules for stabilizing particles and droplets.<sup>22</sup> The particles' growth is processed with the monomer transferring from the bulk oil phase to the particles when they collide with and then are incorporated into monomer droplets. In this protocol, the 4-vinylpyridine acts as an emulsifier for the emulsion formation before polymerization due to its both hydrophilic and hydrophobic characteristics, and simultaneously confers the pH sensi-

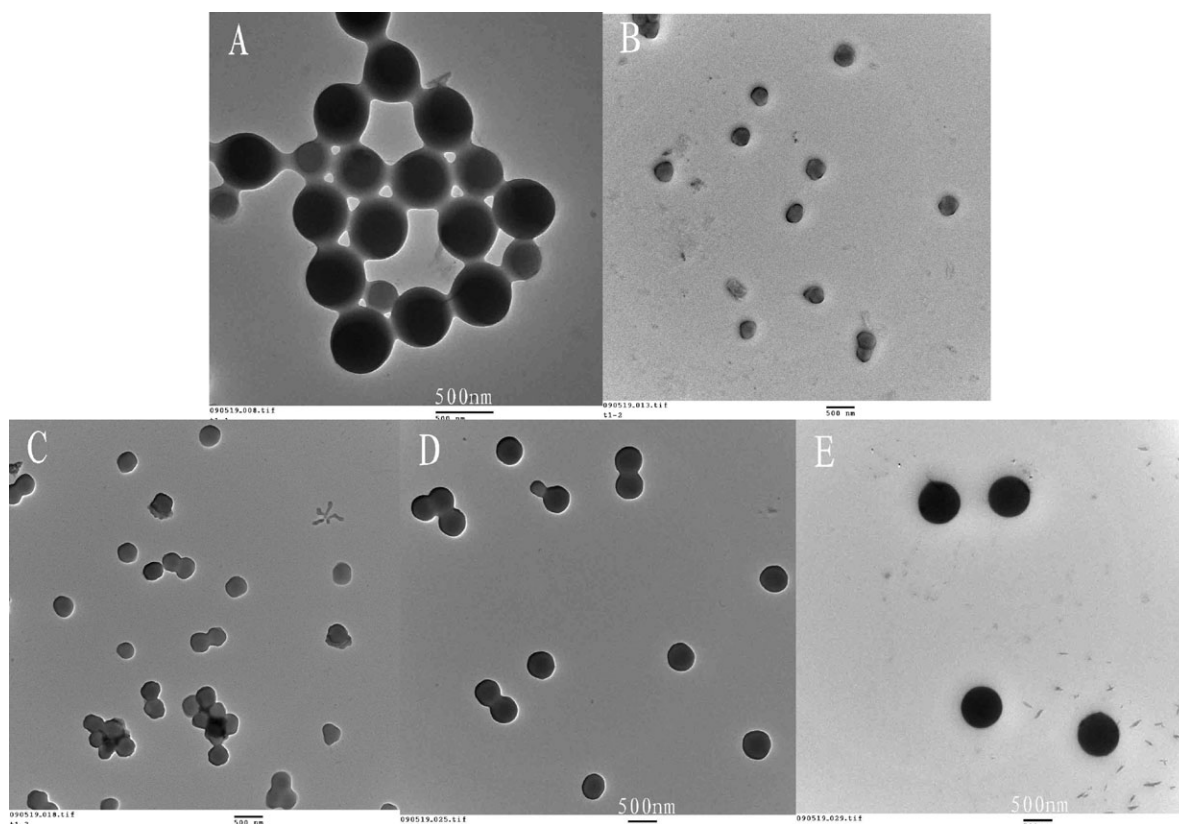
tive properties to the poly (St-co-4VP) spheres after polymerization due to the pH sensitive characters of P4VP segments. The  $K_2S_2O_8$  initiators confer negative charges to the surfaces of the poly (St-co-4VP) spheres by the soap-free emulsion polymerization and thus enhance their dispersal in water.

### Formation of Poly(St-co-4VP) Spheres Through a Stable Soap-Free Emulsion Polymerization

The poly (St-co-4VP) spheres were prepared under a strong stirring condition and the total conversion is larger than 80 wt %. The weight ratio of the crosslinker DVB to monomers was kept constant while that of the 4-vinylpyridine to styrene was varied in the reactive system (Table I). When the 4-vinylpyridine content is low (CSV-10, CSV-82, and CSV-64), the polymerization is stable and no precipitate is observed; but when the 4-vinylpyridine content is high (CSV-46, CSV-28), a small amount of precipitate can be found after the polymerization. In the absence of styrene, a large number of precipitate is observed soon after reaction beginning. The reasons can be interpreted by the soap-free emulsion polymerization mechanism. As mentioned above, the oligomers in the interface of oil/aqueous directly contribute to the formation of particles, whereas the oligomers in aqueous phase mainly provide the surface-active molecules for the stabilization of particles and droplets. In the polymerization system of styrene (CSV-10), the concentration of styrene in aqueous phase is very low, hence only a small quantity of short PS chains with sulfate end groups are generated. These short PS chains are partially adsorbed at the interface of droplet/water and partially phase separated in aqueous phase, leading to the PS spheres formation. At the same time, these short PS chains with sulfate end groups also provide good stabilization for the polymerization like emulsifiers. So the PS spheres without coagulation are prepared. In the polymerization system of 4-vinylpyridine, the 4-vinylpyridine polymerization in aqueous phase is similar to a conventional solution or bulk polymerization where the concentrations of monomer and initiator determine the rate of polymerization and the molecular weight. Because the concentrations of 4-vinylpyridine and  $K_2S_2O_8$  are fairly high in this case, the poly (4-vinylpyridine) chains with high molecular weight will form in a short time. The long poly (4-vinylpyridine) chains become entangled and fast precipitate in aqueous phase. Therefore, the unique way to prepare the stable latex without coagulation is to reduce the concentration of 4-vinylpyridine in aqueous phase as low as possible. Because the solubility of hydrophilic monomer in aqueous phase can be reduced by increasing the amount of hydrophobic monomers in polymerization system,<sup>22</sup> the coagulation-free particles are expected to be prepared by reducing the fraction of 4-vinylpyridine in comonomers. In fact, the coagulation was decreased when the weight ratio of 4-vinylpyridine/styrene was decreased from 8/2 to 6/4 in comonomers (CSV-28, CSV-46). When the weight ratio of 4-vinylpyridine/styrene was further decreased in the reactive system (CSV-64, CSV-82), the stable latex without coagulation was successfully prepared.

### Morphology and Structure of Poly(St-co-4VP) Spheres

The morphologies of the polymeric spheres are observed under TEM and the results are shown in Figure 1. It can be seen that all the particles are spherical morphologies and their sizes are largely affected by the 4-vinylpyridine content in the reactive



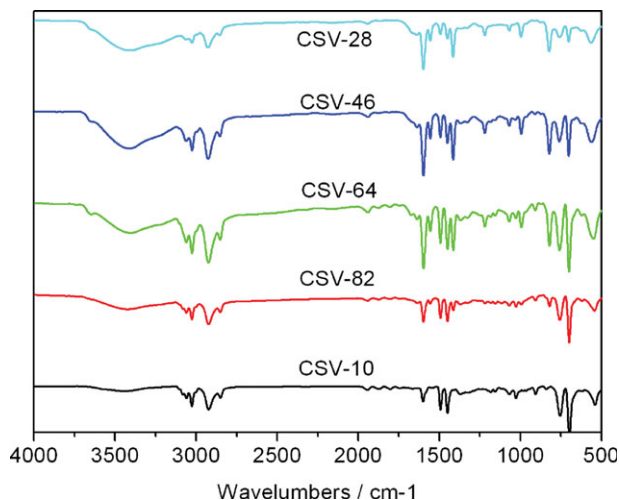
**Figure 1.** TEM micrographs of poly (St-co-4VP) spheres prepared from different components: (A) CSV-10, (B) CSV-82, (C) CSV-64, (D) CSV-46, (E) CSV-28.

system. In the absence of 4-vinylpyridine monomer, the obtained PS spheres show two different sizes [Figure 1(A)]. When the 4-vinylpyridine fractions are in the comonomer feed range of 0.20–0.80, the resultant poly (St-co-4VP) spheres are narrowly distributed [Figure 1(B–E)]. The TEM micrographs are further used to calculate a number average diameter with a coefficient of variation, and the results are summarized in Table I. From Table I, it can be seen that the PS spheres show an average diameter of about 449 nm with one diameter of about 307 nm and another diameter of about 500 nm. The average size of the polymeric sphere firstly decreased from 449 to 340 nm and then increased with increasing 4-vinylpyridine fraction in comonomer (Table I).

The narrow size distribution for the poly(St-co-4VP) spheres can be explained by the reactivity of the primary nucleating particles, which are formed at the initial state of polymerization, towards the surrounding residual monomers.<sup>22,25</sup> In the absence of 4-vinylpyridine, the oligomer radicals of PS are formed in aqueous phase and in the interface of oil/water phase. These oligomer radicals in aqueous phase might phase separate, leading to the initial nucleation; while these oligomer radicals adsorbed at the interface of droplet/water might lead to the droplet nucleation. These nucleating sites then start to capture the surrounding monomers to form the particles. Because styrene is a very hydrophobic monomer, the concentration of styrene in oil phase is very high while that in aqueous phase is very low. The monomer disproportion in aqueous and oil phase

thus results in the different growth rates of nucleating particles and further leads to the broad-distribution PS spheres. The small particles are possibly derived from the phase separation nucleation in aqueous phase, while the larger particles maybe come from the droplet nucleation. In the presence of 4-vinylpyridine, the oligomer radicals of poly (4-vinylpyridine) are formed in aqueous phase and in the interface of oil/aqueous phase. These oligomer radicals in aqueous phase provide the surface-active molecules for the stabilization of particles and droplets but can not lead to the homogeneous nucleation by phase separation.<sup>22</sup> Therefore, only the droplet nucleation formed by the oligomer radicals adsorbed at the interface of droplet/aqueous contributes to the particle formation. Because the averaged equal possibility of collision of per particle, the nucleating particles grow with a similar rate. Therefore, the narrowly distributed poly (St-co-4VP) spheres are formed.

The sizes of the polymeric spheres may be affected by the numbers of nuclei resulted from the oligomers adsorbed in the interface of oil/water phase. A larger number of nuclei formed in the interface of oil/water phase to have the tendency to decrease the particle size. With the increase of 4-vinylpyridine monomers, a large amount of oligomer radicals of poly (4-vinylpyridine) are entangled to precipitate in aqueous phase while a small amount of poly (4-vinylpyridine) oligomer radicals exist in the interface of oil/water.<sup>22</sup> The decrease of the nuclei numbers in the interface resulting from the decreased poly (4-vinylpyridine) oligomers may be related to the formation of poly (St-co-4VP)



**Figure 2.** FTIR spectra of poly(St-co-4VP) spheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

spheres with larger sizes. Therefore, the sizes of the poly (St-co-4VP) spheres increase with increasing 4-vinylpyridine fraction in comonomer (Table I).

The chemical structures of the polymeric spheres are determined by FTIR spectra (Figure 2). The characteristic absorption at  $1556\text{ cm}^{-1}$  is attributed to the asymmetric stretching vibration of C=N in the P4VP segment;  $1607$ ,  $1496$ , and  $1452\text{ cm}^{-1}$  are attributed to the aromatic benzene stretching vibrations of C=C in the copolymers of styrene and divinylbenzene (CSV-10 in Figure 2). The characteristic absorptions attributed to the styrene, divinylbenzene and 4-vinylpyridine are clearly observed in the samples of CSV-82, CSV-64, CSV-46, and CSV-28 (Figure 2), which suggests the polymeric spheres are the copolymers of styrene, divinylbenzene and 4-vinylpyridine. In addition, the characteristic absorption intensity at  $1556\text{ cm}^{-1}$  increases with an increase of 4-vinylpyridine fraction in the reactive system, indicating more 4-vinylpyridine are introduced to the polymeric sphere.

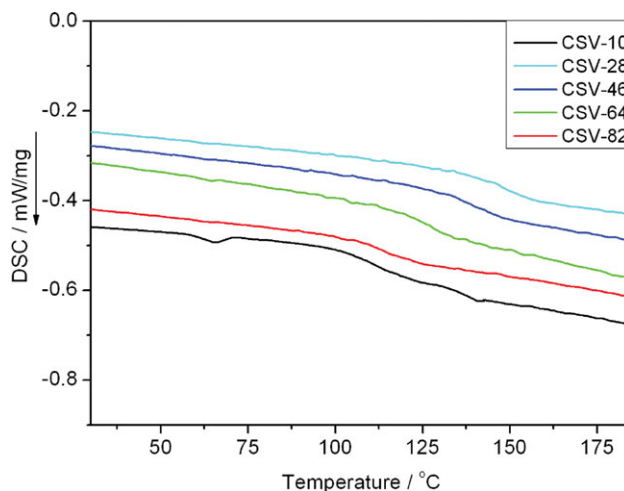
Figure 3 and Table I show the DSC results of the Poly (St-co-4VP) spheres prepared in the systems with a fixed crosslinker level of 3.8 wt % divinylbenzene and various 4-vinylpyridine/styrene ratios. It can be observed that all the Poly (St-co-4VP) spheres show one glass transition behavior which moves to an increasingly higher temperature with increasing 4-vinylpyridine content in reactive system (Figure 3). The  $T_g$ s are affected by the components and crosslinked structures of the polymeric spheres. To know the P4VP and PS segments to the contributions of the  $T_g$ , the homopolymers of styrene and 4-vinylpyridine are respectively synthesized and their  $T_g$ s are measured by the same method described in the experiment part. The  $T_g$  of the PS homopolymer is about  $100^\circ\text{C}$ , smaller than that of the P4VP homopolymer (about  $138^\circ\text{C}$ ). Therefore, the different  $T_g$ s should be partially ascribed to the different components of the Poly (St-co-4VP) spheres. As is expected, the lower  $T_g$  corresponds to the polymeric spheres with a lower content of P4VP; while the higher  $T_g$ , on the other hand, corresponds to the polymeric sphere with a higher content of P4VP (Table I). The

similar results are also reported in the investigation of the uncrosslinked Poly (St-co-4VP) spheres.<sup>23</sup>

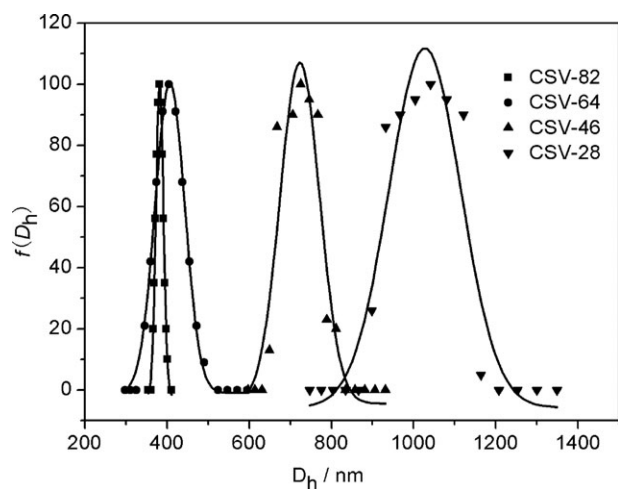
The crosslinker DVB also plays an important effect on the glass transition behavior of the polymeric sphere. The  $T_g$  of the crosslinked PS microsphere is  $109.5^\circ\text{C}$ , larger than that of the PS homopolymer ( $T_g = 100^\circ\text{C}$ ), indicating the crosslinked structure restricts the movement of the PS segment (CSV-10 in Figure 3 and Table I). The crosslinked structure also shows similar effect on the  $T_g$  of the poly(St-co-4VP) sphere. When the 4-vinylpyridine content is relatively high in the reactive system (CSV-46 and CSV-28 in Figure 3 and Table I), the  $T_g$ s of the poly(St-co-4VP) spheres get to  $140.6$  and  $148.8^\circ\text{C}$ , higher than that of the P4VP homopolymers ( $T_g = 138^\circ\text{C}$ ), indicating the movements of the P4VP and PS segments are also restricted by the crosslinked structure.

### pH-Sensitive Properties of Poly(St-co-4VP) Spheres

The Poly (St-co-4VP) spheres are first dispersed in water (pH 7) and their hydrodynamic sizes are determined using DLS. The hydrodynamic diameter ( $D_h$ ) of PS microsphere is  $520\text{ nm}$  (Table I), approaching to the large particle size ( $500\text{ nm}$ ) shown in Figure 1(A), while the  $D_h$  approaching to the small size ( $307\text{ nm}$ ) shown in Figure 1(A) is not detected. This is due to the DLS characterization being much more sensitive to larger particles.<sup>10</sup> The  $D_h$  of the CSV-82 sample is  $380\text{ nm}$ , slightly larger than the size from TEM ( $340\text{ nm}$ ), (Figure 1 and Table I). It is likely that the  $D_h$  shows the swollen state of the particle due to the hydrophilic pyridine segment, while TEM observation shows their dried aggregate state. With the increase of 4-vinylpyridine content, the size measured from DLS is larger than that from TEM (CSV-64 in Figure 4 and Table I). This result is resulted from the increased swollen extent due to the more hydrophilic 4-vinylpyridine segment introduced. With a further increase of 4-vinylpyridine, the size measured from DLS becomes much larger than that from TEM (CSV-46 and CSV-28 in Figure 4 and Table I). This is possibly resulted from the increased swollen extent due to the more hydrophilic 4-vinylpyridine segments



**Figure 3.** The DSC thermograms of the poly(St-co-4VP) spheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



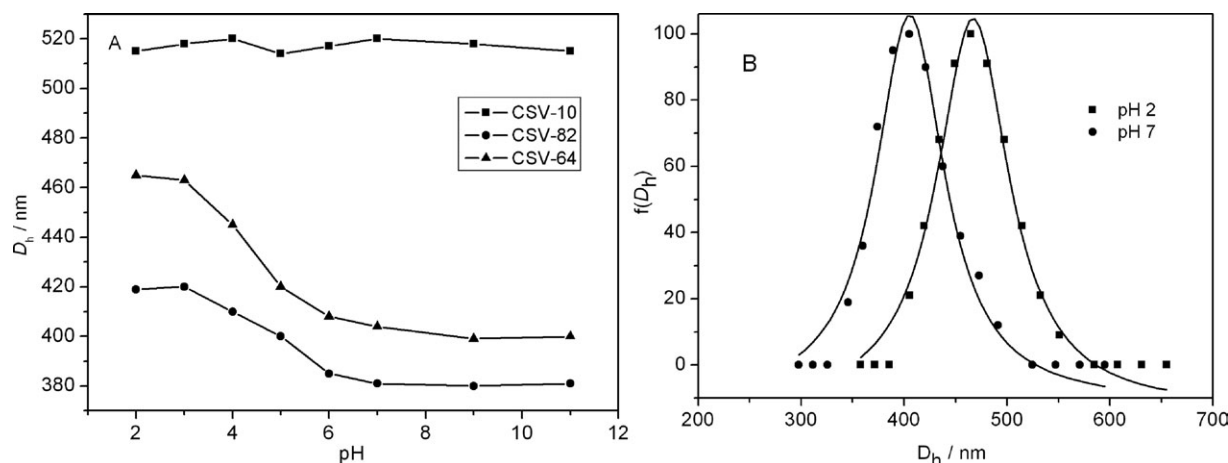
**Figure 4.** Hydrodynamic diameter distributions of poly(St-co-4VP) at pH 7.

introduced, but more possibility could be the aggregation of the Poly (St-co-4VP) spheres in water due to their large sizes.<sup>7</sup> It is well-known that P4VP chains have distinct hydrophilic and hydrophobic properties closely corresponding to their pH environments. Under a low pH condition, the P4VP segments have good hydrophilic property and can be well swollen in water. Increasing pH value will induce weaker hydrophilic property but stronger hydrophobic property. As the P4VP segments are not largely protonated in water (pH 7), the Poly (St-co-4VP) spheres are not enough stabilized by the negative charges come from the decomposition of the potassium persulfate and thus appear aggregation. Therefore, the DLS results show much larger sizes and wider size distributions (CSV-46 and CSV-28 in Figure 4).

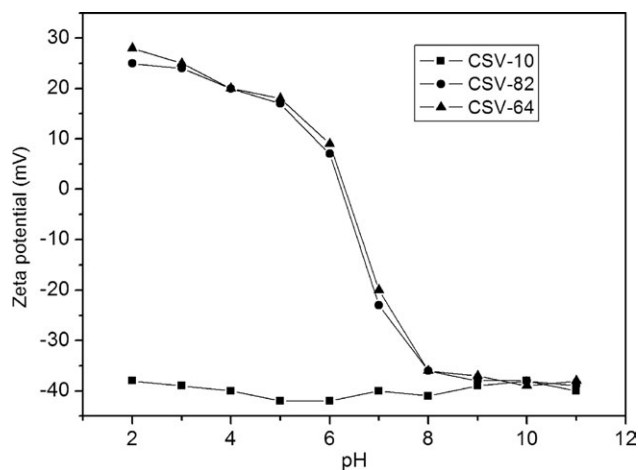
The pH-sensitive properties of the crosslinked polymeric spheres are investigated by measuring their sizes in water with different pH values. To eliminate the effect of the particles aggregation on the DLS results, the CSV-64, CSV-82 and CSV-10 samples are selected and the DLS results are shown in Figure 5(A). It can be

seen that the CSV-82 and CSV-64 samples show an obvious pH-dependent size in water. Under a low pH condition (pH < 3), the CSV-82 and CSV-64 particles show large sizes; increasing pH from 3 to 6, the hydrodynamic sizes abruptly decrease with an increase of pH; further increasing pH from 7 to 11, the hydrodynamic sizes keep constant. The hydrodynamic sizes affected by pH values are a reflection of swollen degree change of the polymeric spheres.<sup>26</sup> Under a low pH condition (pH < 3), due to large protonation of the P4VP segments, the poly(St-co-4VP) spheres are swollen and thus show the large hydrodynamic sizes. With an increase of pH (pH 3–6), due to the partial deprotonation of P4VP segments, the swollen degree of Poly (St-co-4VP) spheres decreases and the corresponding particles show smaller sizes. Under high pH conditions (pH > 7), since the P4VP segments are almost completely deprotonated, the polymeric spheres thus show the smallest sizes. The sizes of the CSV-82 and CSV-64 samples measured under different pH conditions are all larger than those from the TEM observations, the possible reason is that the DLS results come from the wetting state where the CSV-82 and CSV-64 samples are swollen, while the TEM results come from the dried state where the CSV-82 and CSV-64 samples are contracted.<sup>27</sup> The typical size distributions of the CSV-64 samples in pH 2 and 7 are shown in Figure 5(B). The similar size distributions of the poly(St-co-4VP) spheres under both pH conditions indicate that the polymeric spheres are well dispersed and their size differences are ascribed to the different swollen degree. The size change of the CSV-82 sample in water is small than that of the CSV-64 sample, possibly due to the small change of the swollen degree resulted from the low P4VP content in the poly(St-co-4VP) spheres. The effect of the negative charges on the DLS results is detected by measuring the sizes of the blank sample CSV-10 in water with different pH values. Almost no obvious size difference is found under different pH conditions, indicating the influence of the negative charges to the  $D_h$ s of the polymeric spheres can be neglected.

Aqueous electrophoresis studies of the CSV-10, CSV-82, and CSV-64 samples are carried out as a function of pH and the results are shown in Figure 6. It can be seen that the  $\zeta$  potential



**Figure 5.** Hydrodynamic diameters of poly(St-co-4VP) spheres at different pH values (A) and the typical diameter distributions of CSV-64 particles at pH 2 and pH 7 (B).



**Figure 6.** Electrophoretic mobility vs. pH curves obtained for 0.01 wt % aqueous solutions of poly(St-co-4VP) spheres.

data of CSV-82 and CSV-64 samples show a classical “S” shape, being positive at low pH and negative at high pH. The CSV-82 and CSV-64 particles exhibit isoelectric points (IEP) ranging from pH 6.0 to 7.0, and their isoelectric point is estimated to be around 6.2. The poly(St-co-4VP) spheres possess one cationic (pyridine) and one anionic (sulfate) ionizable surface groups. The sulfate groups, originating from the persulfate initiator, are ionized over a wide range of pH (CSV-10 in Figure 6). Hence, the CSV-82 and CSV-64 samples are cationic at low pH due to protonation of the pyridine groups, but become anionic at high pH owing to their ionized sulfate groups. These  $\zeta$  potential results further confirmed the pH-sensitive behavior of the poly(St-co-4VP) spheres was a protonation/deprotonation consequence of their pyridine group.

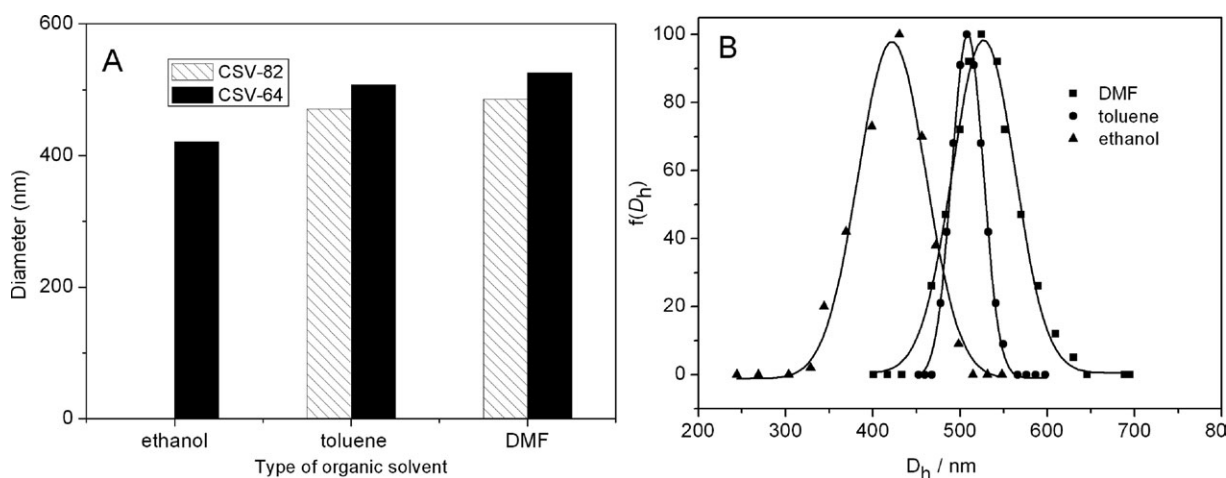
### Organic Solvent Sensitive Property of Poly(St-co-4VP) Spheres

The organic solvent-sensitive properties are checked out by respectively measuring the hydrodynamic diameters of CSV-82

and CSV-64 samples in ethanol, toluene and DMF, and the results are shown in Figure 7(A). The hydrodynamic diameters of the CSV-82 and CSV-64 samples show an increased tendency in term of the solvent order of ethanol, toluene and DMF (the dynamic size of CSV-82 in ethanol was not detected because it can't be dispersed in this solvent.). The results may be explained by the different swollen behaviors of the polymeric spheres in organic solvents where the whole interaction between a polymer segment and a solvent is resulted from the disperse, polar, and hydrogen-bonding interactions described by the solubility parameters.<sup>28</sup> For the nonpolar PS segments, those nonpolar solvents having solubility parameters approaching to that of the PS will well swell them. Toluene is a nonpolar solvent (Table II), the polymer-solvent interaction between PS and toluene is strong and therefore PS segments are well swollen in this solvent.<sup>24,28</sup> For the polar P4VP segments, the polar parameter and the hydrogen-bonding parameter (Table II) have a large effect on the polymer-solvent interactions. Ethanol has similar values of the polar Hansen parameter and hydrogen-bonding Hansen parameter (Table II), the polymer-solvent interaction between the polar P4VP segment and ethanol is strong and thus the P4VP will be well swollen in ethanol. Because the PS and P4VP segments are only well swollen by toluene and ethanol, respectively, and furthermore, the content of PS segments is higher than that of P4VP segments in the CSV-82 and CSV-64 particles, the particles are well swollen and thus show a larger size in toluene. Although the solubility parameters of DMF, PS segments and P4VP segments are very different, both the PS and P4VP segments are well swollen by DMF.<sup>27,28</sup> So the DLS results show the largest sizes as the CSV-82 and CSV-64 samples are dispersed in DMF. It should be noted that the sizes of the CSV-64 samples in ethanol measured by DLS are larger than in pH 7 water but smaller than in pH 2 water (Figure 5). The possible reason is that the swollen degree of the CSV-64 samples is larger in ethanol than in pH 7 water, but smaller than in pH 2 water.

### Structure Stability of Poly(St-co-4VP) Spheres

Because toluene and ethanol are respectively the solvents for polystyrene and poly(4-vinylpyridine), they possibly destruct



**Figure 7.** Hydrodynamic diameter of CSV-82 and CSV-64 particles in different solvents (A) and the typical hydrodynamic diameter distributions of CSV-64 particles. TEM micrographs of CSV-64 particles treated by toluene (A) and ethanol (B).

the structure of the spheres by extracting the uncrosslinked polystyrene and poly (4-vinylpyridine) segments. Similarly, DMF is the solvent for both polystyrene and poly (4-vinylpyridine) and can destruct the structure of the sphere by extracting the uncrosslinked homopolymers or copolymers of them. Thus, the structure stability of the poly (St-co-4VP) spheres may be evaluated by examining their resistance to toluene, ethanol and DMF. Because CSV-82 samples can not be dispersed into ethanol, the CSV-64 samples are used to examine their resistance to toluene and ethanol. Figure 8 showed the morphologies of CSV-64 samples in their dried state after they were treated by toluene and ethanol. Comparison with the results shown in Figure 1(C), the CSV-64 samples still exhibited spherical shape and similar sizes, suggesting the structures of the CSV-64 particles are stable in these two organic solvents. Because the carbon film was destructed by DMF when the CSV-64 suspension in DMF is deposited onto a carbon film-coated copper EM grid, the observation of the dried CSV-64 samples after being treated by DMF is failed. The structure stability of the CSV-64 samples is thus checked out by comparing their dried weight after and before being continuously extracted for 24 h with DMF. Considering DMF is a good solvent for swelling PS and P4VP segments, the larger value of the weight ratio indicates the destruction is small and the structure stability is better. The weight ratio of the CSV-64 samples after and before being extracted is 100/99, indicating the poly (St-co-4VP) spheres have good structure stability in DMF. No weight change is found after the CSV-82 samples are extracted by the same method, indicating the structure of the polymeric sphere is also stable in DMF.

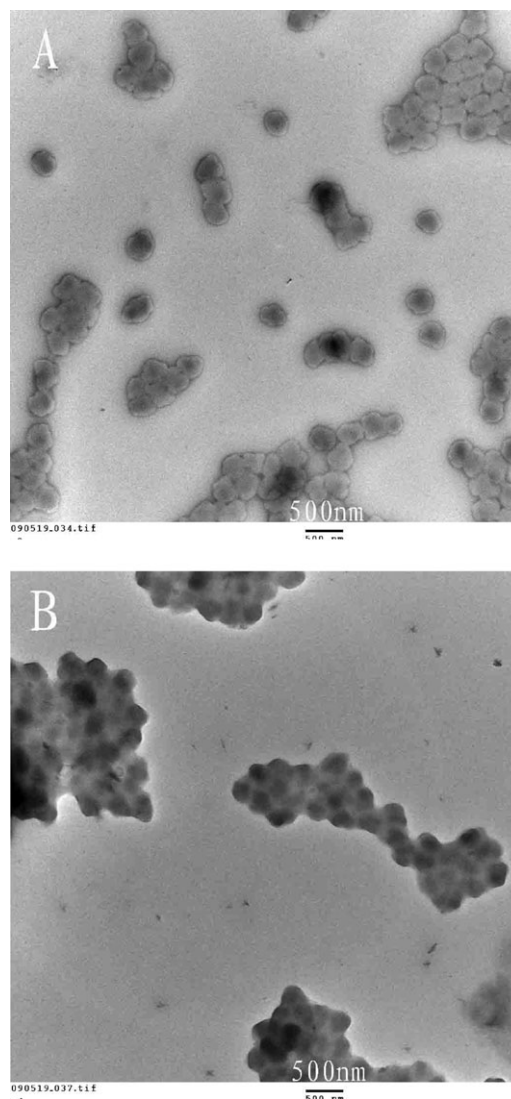
## CONCLUSIONS

Poly (St-co-4VP) spheres with different compositions are prepared by a soap-free emulsion polymerization in water in the presence of styrene, 4-vinylpyridine and DVB. The 4-vinylpyridine acts as a comonomer and emulsifier, favoring more uniform spheres formation. The obtained poly(St-co-4VP) spheres have cross-linked structures and keep good structure stability in water, ethanol, toluene and DMF. When the weight ratio of 4-vinylpyridine to styrene is less than 4/6 in reactive system, the obtained poly (St-co-4VP) spheres show pH-sensitivity in water. Under a low pH condition (pH 2), the poly (St-co-4VP) spheres show larger sizes; increasing pH value, their sizes change

**Table II.** Solubility Parameters of the Solvents and Polymers<sup>28</sup>

Solvent or polymer	$\delta_{\text{total}}$ (MPa <sup>1/2</sup> )	$\delta_{\text{d}}$ (MPa <sup>1/2</sup> )	$\delta_{\text{p}}$ (MPa <sup>1/2</sup> )	$\delta_{\text{h}}$ (MPa <sup>1/2</sup> )
PS	19.0	18.6	1.0	4.1
P4VP	20.6	18.1	7.2	6.8
Toluene	18.2	18.0	1.4	2.0
Ethanol	26.5	15.8	8.8	19.4
DMF	24.8	17.4	13.7	11.3

$\delta_{\text{total}} = (\delta_{\text{d}}^2 + \delta_{\text{p}}^2 + \delta_{\text{h}}^2)^{1/2}$ ,  $\delta_{\text{total}}$  = total solubility parameters,  $\delta_{\text{d}}$  = disperse Hansen parameter,  $\delta_{\text{p}}$  = polar Hansen parameter,  $\delta_{\text{h}}$  = hydrogen-bonding Hansen parameter.



**Figure 8.** TEM micrographs of CSV-64 particles treated by toluene (A) and ethanol (B).

smaller. When the weight ratio of 4-vinylpyridine to styrene is 4/6 in reactive system, the poly (St-co-4VP) spheres also show obvious solvent-sensitive characters. Especially speaking, the poly (St-co-4VP) spheres show larger sizes in DMF, a smaller size in toluene and the smallest size in ethanol. All the solvent-sensitive characteristics are closely related to the swollen property of the poly (St-co-4VP) spheres.

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