Front. Chem. China 2009, 4(1): 83–88
DOI 10.1007/s11458-009-0003-1

RESEARCH ARTICLE

Linfeng ZHAI, Tiejun SHI, Hualin WANG

Preparation of polyvinylpyrrodione microspheres by dispersion polymerization

Abstract The preparation of polyvinylpyrrolidone (PVP) microspheres in ethyl acetate by dispersion polymerization with *N*-vinylpyrrolidone (NVP) as initial monomer, poly(*N*-vinylpyrrolidone-co-vinyl acetate) (P(NVP-*co*-VAc)) as dispersant, and 2, 2′-azobisisobutyronitrile(AIBN) as initiator is reported. The influences of monomer concentration, dispersant concentration and initiator concentration on the size of PVP microspheres as well as the monomer conversion were studied. The structure and properties of PVP microspheres were analyzed. The results show that the prepared PVP microspheres have a mean diameter of 3–4 μm. With an increase in NVP concentration, the size and the molecular weight of the PVP microspheres as well as the monomer conversion all increase. With increasing P(NVP-*co*-VAc) concentrations, the PVP molecular weight and monomer conversion both increase while the size of the microspheres becomes smaller. As the concentration of AIBN increases, the microsphere size and monomer conversion increase whereas the PVP molecular weight decreases. The PVP prepared by dispersion polymerization has a crystal structure, and its molecular weight is lower compared to that prepared by solution polymerization.

Keywords polyvinylpyrrolidone, microsphere dispersion polymerization, preparation

Polyvinylpyrrolidone (PVP) is a kind of valuable green polymer with good solubility, film formation, biocompatibility and chemical stability. PVP is widely used in medicine, cosmetics, foodstuff, paints, adhesives and photosensitive materials [1,2]. PVP can be prepared by bulk polymerization [3] or solution polymerization [4,5] with N-vinylpyrrolidone (NVP) as raw material. Since the viscosity of the reaction system in bulk polymerization is very high, the polymer can not diffuse freely, and it is difficult to remove the heat. Therefore, the PVP product usually has a low molecular weight and has high residual monomer content. Bulk polymerization has scarcely been applied in industry [6]. Nowadays, the production of PVP by the solution polymerization process is the most common way. However, the difficulty in solvent recycling, broad molecular weight distribution and the additional spray drying process for powder formation have restricted the applications of this method.

Dispersion polymerization is a polymerization technique that was set up in the 1970 s. Compared to other polymerizations, dispersion polymerization has unique advantages: the polymerization technology is simple, the polymerization heat can be easily removed, and the process is applicable to all kinds of monomers [7]. Many studies on the nucleation mechanism and kinetics of dispersion polymerization have been reported, and most of them employ hydrophobic monomers such as styrene (St) and methyl methacrylate (MMA) [10,11]. In comparison, there are only a few literatures available on dispersion polymerization of hydrophilic monomers such as acrylic acid (AA) and acrylamide (AM) [12–14]. For the amphoteric monomer NVP, it is very hard to find an appropriate dispersion medium and dispersant. Up to now, PVP microspheres have been successfully prepared only by dispersion polymerization in supercritical carbon dioxide [15].

As an amphoteric polymer, PVP is soluble in polar organic solvents but is hardly soluble in low polar or non-polar solvents. Also, the molecular weight of PVP significantly influences its solubility. In high polarity solvents, the solubility of PVP decreases with the increase in its molecular weight. In non-polar solvents, the solubility of PVP is very low and changes slightly with its molecular weight. The dispersion medium is not only a solvent for the dispersant, initiator and monomer, but is also a non-solvent for the polymer formed in the reaction. In this paper, we describe the preparation of PVP

Translated from *Acta Polymerica Sinica*, 2007, 11 (in Chinese)

Linfeng ZHAI (✉), Tiejun SHI, Hualin WANG
School of Chemical Technology, Hefei University of Technology, Hefei 230009, China
E-mail: zhai-lf@sohu.com

microspheres by dispersion polymerization. The low-toxicity solvent ethyl acetate was chosen as the reaction medium. The reaction conditions that affected the PVP microsphere size and molecular weight as well as the conversion efficiency of NVP were studied, and the cause of PVP microspheres having a crystal structure was analyzed. Our work developed a new method for PVP microsphere preparation, which was of great potential in the PVP preparation industry.

1 Experiments

1.1 Materials

NVP (Henan Boai Fine Chemical Industry, > 99.9 wt%) was purified by vacuum distillation before use. We prepared Poly(*N*-vinylpyrrolidone-*co*-vinyl acetate)(P(NVP-*co*-VAc)) ($M_V = 8 \times 10^4$) by ourselves. 2, 2′-Azobisisobutyronitrile (AIBN, Shanghai Chemicals Forth-Plant, China) was purified by recrystallization from ethanol. Other reagents were of AR grade and used as received.

1.2 Preparation of PVP microspheres

0.4 grams of P(NVP-*co*-VAc) was dissolved in 80 grams of ethyl acetate under constant stirring in a water bath at 70°C, and then 20 grams NVP and 0.15 grams AIBN were added in. The polymerization was conducted under nitrogen atmosphere for 6 hours. The mixture was cooled down and then filtrated, and the insoluble matter was vacuum dried at room temperature for 24 h to get white powders.

1.3 Characterization

The functional groups of the samples were characterized by Fourier-transform infrared spectroscopy (FT-IR). The sample was ground with dried potassium bromide (KBr) powder and compressed into a disc. The crystal structure of PVP was determined by powder x-ray diffraction spectroscopy (D/max-γ B). The thermal stability of PVP was determined by differential scanning calorimeter (Mettler Toledo DSC-821E). The heating rate was 10°C/min in a nitrogen atmosphere. The recorded temperature range was 25–300°C. The morphology of the PVP microspheres was observed by optical microscope (XSP-XSZ).

For the determination of monomer residue and viscosity-average molecular weight of PVP, refer to Ref. [6]. The conversion of NVP was calculated using the following equation:

$$\text{Conversion}(\%) = \left(1 - \frac{\text{Re sidue } NVP}{\text{Initial } VP}\right) \times 100\%$$

2 Results and discussion

2.1 Effect of the initial monomer concentration

Figure 1 shows the photomicrographs of the PVP microspheres, which were prepared using different initial monomer NVP concentrations. The PVP microspheres dispersed well in ethyl acetate, and no agglomeration appeared among the microspheres. When the initial monomer concentration was 20 wt%, uniform PVP microspheres with a mean diameter of 4 μm were obtained. The higher the initial monomer concentration was, the larger the size of the PVP microspheres was. When the initial monomer concentration was 30 wt%, the mean size of the microspheres reached 6 μm, and the particle size distribution became broader. As the initial monomer concentration increased, the chain length of the oligomeric precipitates increased and the number of the formed nucleates decreased. It may have led to the larger size of the PVP particles. On the other hand, in the case of higher monomer

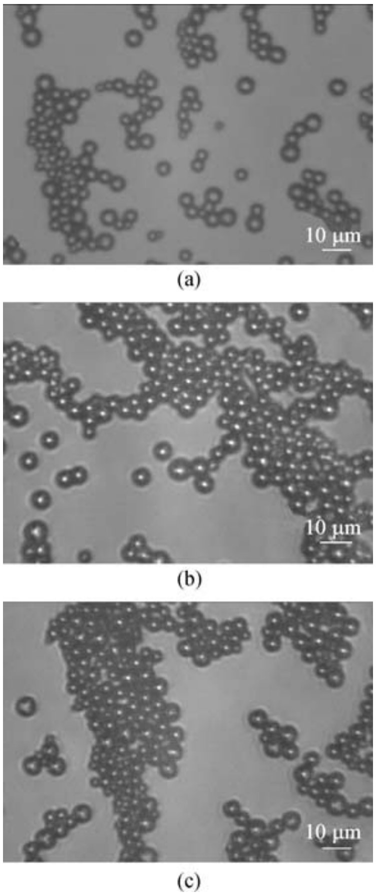

Fig. 1 Effect of initial monomer concentration on the size of PVP particles. [Dispersant] = 2 wt%; [AIBN] = 0.75 wt%; Temperature = 70°C. (**a**) 20 wt%; (**b**) 25 wt%; (**c**) 30 wt%

concentrations, the oligomeric radicals in solution could have continued to aggregate to generate more new particles and resulted in a broader size distribution.

Figure 2 shows the curves of the monomer conversion versus time with various NVP monomer concentrations. It can be seen that the reaction rate was rapid at the beginning of the dispersion polymerization, and then slowed down after being sustained for a short time. Generally speaking, the conversion of the monomer increased with the increase inn its concentration.

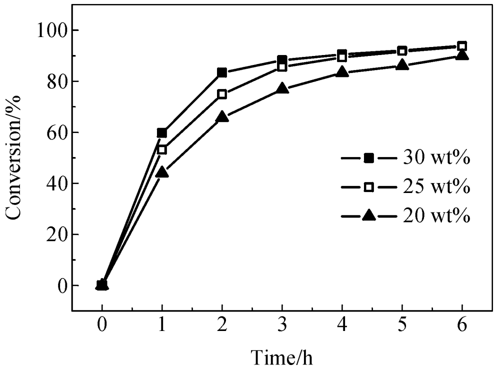

Fig. 2 Conversion vs time with various NVP monomer concentrations. [Dispersant] = 2 wt%; [AIBN] = 0.75 wt%; Temperature = 70°C

Dispersion polymerization starts as a solution polymerization reaction. The polymerization initially occurs in the homogeneous solution and thus oligomer radicals are formed. When the polymer chains grow to a critical length, they begin to precipitate from the reaction medium, resulting in primary nuclei. This process is regarded as the nucleation stage, and this stage is very short. The concentration of the formed nuclei is high, the size is large, and moreover there are more monomers absorbed in the nuclei. In the subsequent particle growing stage, the size of the particles increases as the monomers in the nuclei polymerize, and the exiting particles capture the free monomers in the reaction medium. Hence, the increase in monomer concentration is of advantage to the polymerization of the monomers, and can also improve the efficiency of the particles in capturing the monomers in the liquid phase. Thereby, the polymerization rate and the conversion increase. During the reaction, the monomer concentration and the reaction rate decrease, and the conversion tends to increase slowly.

Table 1 shows the effect of concentrations of monomer, dispersant and initiator on the viscosity molecular weight of PVP. When the monomer concentration was in a certain range, the viscosity molecular weight of PVP increased gradually along with the monomer concentration.

2.2 Effect of the dispersant concentration

Figure 3 shows the microscope photomicrographs of PVP microspheres prepared with different dispersant concentrations. The dispersant has a great effect on the size of PVP microspheres. With the decrease in dispersant concentration, the size of PVP microspheres increased and the size distribution of the particles broadened. When the dispersant concentration shifted form 1.75 wt% to 1 wt%, the shape of the PVP microspheres turned from original pellets to oval or irregular spheres. Under constant initiator and monomer concentrations, the decrease in dispersant concentration led to decreased dispersant stability. The collision and coagulation among part particles caused the increased size of PVP microspheres. When the size of PVP microspheres exceeded a critical point, the dispersant lost its stability. The violent coagulation among particles made the final particles appear as oval or irregular spheres, and the distribution of the particle size broadened.

Figure 4 gives the curves of the monomer conversion versus time with various dispersant concentrations. The conversion of NVP increased very slowly without dispersants. In our experiments, no phase separation was observed within 6 hours in the reaction, and the polymerization was just a solution polymerization. As the dispersant concentration increased, the monomer conversion also increased. For a same reaction medium, the reaction kinetics of the dispersion polymerization was different from the solution polymerization due to the crucial role of dispersant. In the early stage of dispersion polymerization, a lot of primary particles were formed with the dispersant. It was similar to bulk polymerization when the high concentration monomers absorbed in the primary particles polymerized. On the other hand, the separation of the particles to free radicals slowed the chain termination rate, and the ability of the particles to catch radicals increased as the size of the particles increased. Therefore the dispersion polymerization rate surpassed the solution polymerization rate.

Table 1 Effect of concentration of monomer, dispersant and initiator on M_V of PVP

Molecular weight	Monomer concentration /% [a]			Dispersant concentration /% [b]			Initiator concentration /% [c]		
	20	25	30	0	1.5	2.0	0.5	0.75	1.0
$M_V \times 10^{-4}$	3.2	3.8	4.4	0.3	2.5	3.8	4.1	3.8	3.1

[a] [Dispersant] = 2 wt%, [AIBN] = 0.75 wt%, Temperature = 70°C, Time = 6 h

[b] [PVP] = 25 wt%, [AIBN] = 0.75 wt%, Temperature = 70°C, Time = 6 h

[c] [PVP] = 25 wt%, [Dispersant] = 2 wt%, Temperature = 70°C, Time = 6 h

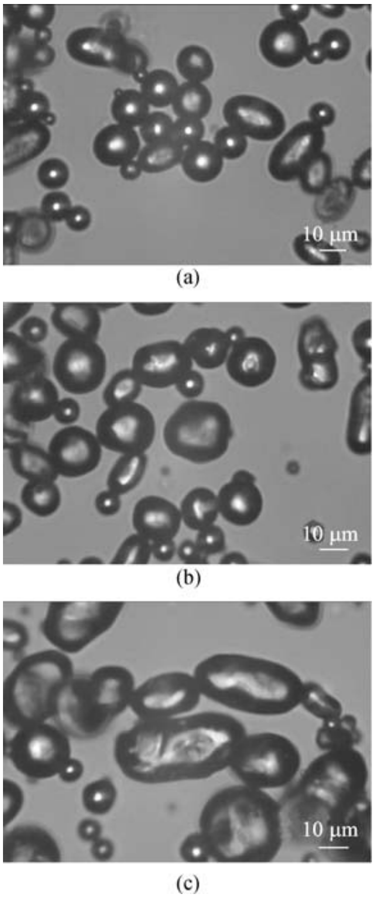

Fig. 3 Effect of dispersant concentration on the size of PVP particles. [PVP] = 25 wt%; [AIBN] = 0.75 wt%; Temperature = 70°C **(a)** 1.75 wt%; **(b)** 1.5 wt%; **(c)** 1.0 wt%

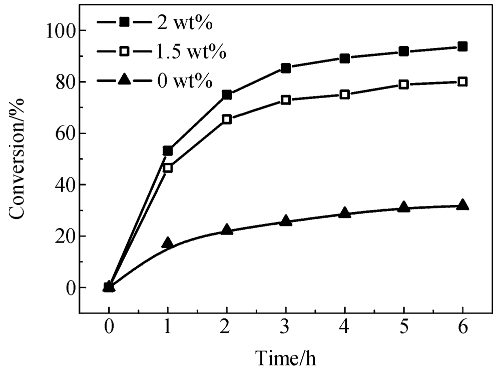

Fig. 4 Conversion vs time with various dispersant concentration. [PVP] = 25 wt%; [AIBN] = 0.75 wt%; Temperature = 70°C

Table 1 shows that when the dispersant concentration was in a certain range, the viscosity molecular weight of PVP increased gradually as the dispersant concentration increased.

2.3 Effect of the AIBN concentration

Figure 5 shows the microscope photomicrographs of PVP microspheres prepared using different initiator concentrations. As the initiator concentration increased, the size of the PVP microspheres increased, and its distribution broadened. In the early stage of the polymeric reaction, increasing the initiator concentration caused an increase in the number of living polymer chains. This may lead to an increase in the polymer particle number (more nuclei) in the reaction medium. For the same dispersant concentration, the probability of the collision and coagulation among the particles increased. These factors may result in the size increase and the size distribution broadening of PVP microspheres.

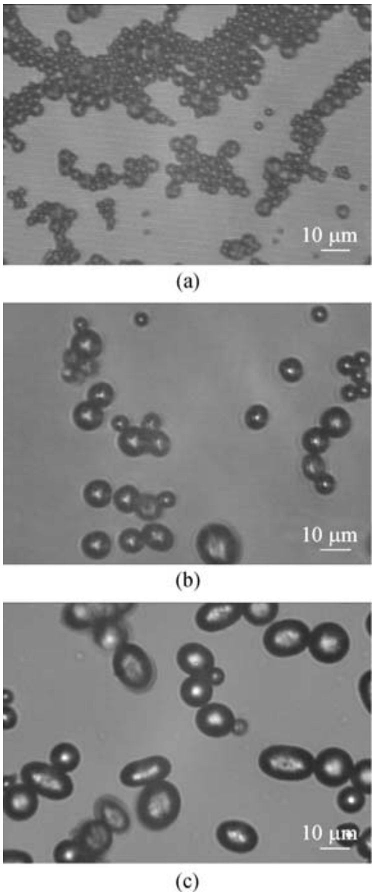

Fig. 5 Effect of initiator concentration on the size of PVP particles. [PVP] = 25 wt%; [Dispersant] = 2 wt%; Temperature = 70°C
(a) 0.5 wt%; **(b)** 1.0 wt%; **(c)** 1.25 wt%

Figure 6 shows the curves of the conversion versus time with various initiator concentrations. It can be seen from

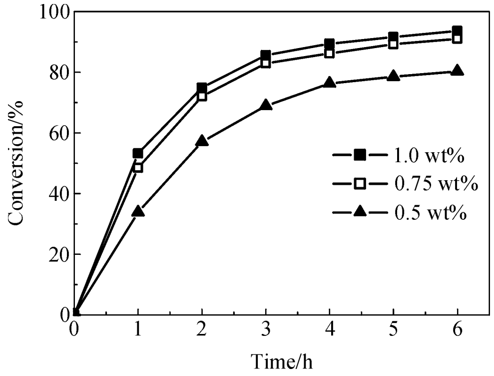

Fig. 6 Conversion vs time with various initiator concentration. [PVP] = 25 wt%; [Dispersant] = 2 wt%; Temperature = 70°C

Fig. 6 that the reaction rate decreased gradually as the monomer concentration decreased along with the reaction time.

Table 1 shows that when the initiator concentration was in a certain range, the viscosity molecular weight of PVP decreased gradually as the initiator concentration increased.

2.4 FT-IR analyses

Figure 7(a) shows the FT-IR spectra of NVP; the characteristic peak at 1703 cm^{-1} is assigned to carbonyl groups, while the characteristic peaks at 3110, 1630 and 1280 cm^{-1} are assigned to olefin groups. Figure 7 (b) shows the FT-IR spectra of PVP microspheres. Compared with Fig. 7(a), the olefin characteristic peaks at 3110 and 1630 cm^{-1} disappear, implying that the olefin of NVP has polymerized to PVP.

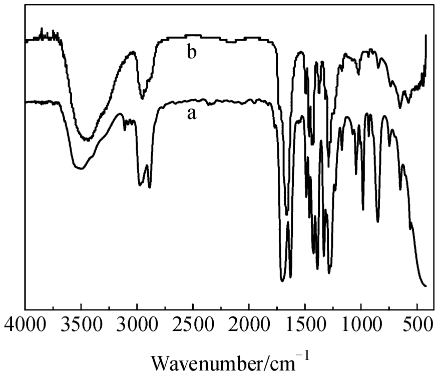

Fig. 7 FT-IR spectra. **(a)** NVP; **(b)** PVP

2.5 XRD and DSC analyses

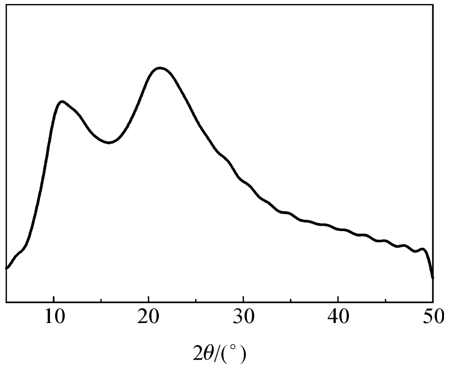

Fig. 8 XRD spectra of PVP

Figure 8 shows the XRD spectra of PVP microspheres prepared by dispersion polymerization. The diffraction peaks at 2θ of 11.66° and 21.04° indicate that the PVP microspheres prepared by dispersion polymerization are crystalline. Fig. 9 shows the DSC curve of PVP microspheres prepared by dispersion polymerization. There is an endothermal peak at 130°C, and no glass transition temperature was found. This also indicates the existence of a crystalline structure. The above results are quite different from those of earlier investigations reporting that the PVP prepared by solution polymerization was an amorphous polymer [16].

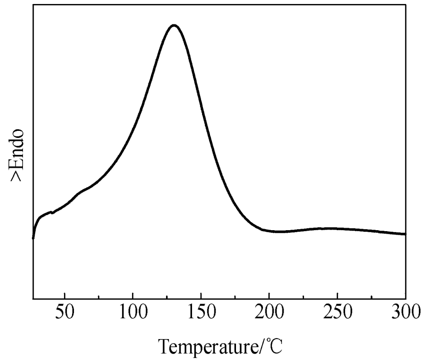

Fig. 9 DSC curve of PVP

PVP is a non-ionic water-soluble polymer with an intralactam. The amide bond is coplanar because the C–N bond has partly double bond characteristics, and a strong hydrogen bond is formed between NH and C=O bonds. Therefore, PVP may have a crystal structure. According to the dispersion mechanism, the monomer reacts with the initiator radicals to form oligomeric radicals, which precipitate as small nuclei at a critical chain length with the dispersant. These nuclei absorb monomers and free radicals from the continuous phase. The monomers polymerize in the swollen nuclei, just like bulk polymerization, to form particles. The number of active radicals in a particle is small, and the probability of having the molecule chain form side chains is also low, which results in the high order degree of the PVP molecules. At the same time, the molecular weight of PVP is low. Therefore, the PVP thus obtained has a crystal structure. PVP prepared by solution polymerization may have a high molecular weight and wide molecular weight distribution, and the number of grafts on its side chains is large. Hence, the disorder degree of the PVP molecules increases, and the final product exhibits an amorphous structure.

3 Conclusion

Monodispersed PVP microspheres, 3–4 μm in size, were successfully prepared in ethyl acetate with NVP as initial monomer, P(NVP-*co*-VAc) as dispersant, and AIBN as initiator. As the concentration of NVP increases, the size and the molecular weight of the PVP microspheres increases, and the monomer conversion rate also increases. As the concentration of AIBN increases, the size of microspheres and the monomer conversion increases, while the molecular weight of PVP decreases. As the concentration of P(NVP-*co*-VAc) increases, the molecular weight of PVP and the monomer conversion rate increases, whereas the microsphere size decreases. The molecular weight of the PVP microspheres prepared by dispersion polymerization ranges from 2.5×10^4 to 4.4×10^4, while the molecular weight of PVP prepared by solution polymerization is about $3260–8.0\times10^5$ [6]. The PVP prepared by dispersion polymerization has a crystal structure and its molecular weight is lower compared to that prepared by solution polymerization.

Acknowledgements This work was financially supported by the Technology Research Foundation of Hefei University (No. 060607F).

References

1. Haaf F, Sanner A, Straub F. Polymer on N-vinylpyrrolidone: synthesis, characterization and uses. Polymer Journal, 1984, 17(1): 143–152
2. Yan Ruixuan. Water-Soluble Polymers. Beijing: Chemical Industry Press, 1998, 586–689
3. Cui Y D, Yi G B, Liao L W, Kang Z. Radical polymerization of N-vinlpyrrolidone in solution. Journal of Chemical Industry Engineering, 2000, 51(3): 369–371 (in Chinese)
4. Senogles E, Thomas R A. Hydrogen bonding effects in the polymerization of N-vinylpyrrolidone. Journal of Polymer Science, Polymer Letters Edition, 1978, 16(11): 555–562
5. Panarin E F, Ushakova V N, Leiukh A I, Kirukhin D P, Munikhes V M. Radiation-induced polymerization of N-vinylpyrrolidone in bulk, in aqueous and alcohol solution. Radiation Physics and Chemistry, 1994, 43(5): 509–513
6. Cui Y D, Yi G B, Liao L W. Synthesis and Application of Polyvinylpyrrolidone. Beijing: Science Press, 2001, 120–207
7. Pojman J A, Gunn G, Patterson C, Owens J, Simmons C. Frontal dispersion polymerization. Journal of Physical Chemistry B, 1998, 102(20): 3927–3929
8. Lee J, Ha J U, Choe S, Lee C S, Shim S E. Synthesis of highly monodisperse polystyrene microspheres via dispersion polymerization using an amphoteric initiator. Journal of Colloid and Interface Science, 2006, 298: 663–671
9. Wang W, Liu L Y, Huang Z H, Yang W T. Study on photoinitiated dispersion polymerization of acrylamide by using poly(acrylic acid)-graft-nonylphenoxypoly- (ethylene oxide) as the dispersant. Acta Polymerica Sinica, 2005, (3): 320–326 (in Chinese)
10. Zhang H T, Yuan X Y, Huan J X. Study of kinetics and nucleation mechanism of dispersion copolymerization of methyl methacrylate and acrylic acid. Reactive & Functional Polymers, 2004, 59: 23–31
11. Lacroix-Desmazes P, Guillot J. Dispersion polymerization of styrene in ethanol-water media: monomer partitioning behavior and locus of polymerization. Journal of Polymer Science, Part B: Polymer Physics, 1998, 36(2): 325–335
12. Murray P G, Ramesh M. Water soluble polymers produced by homogeneous dispersion polymerization. ACS Symposium Series, 2000, 755: 36–45
13. Macková H, Horák D. Effects of the reaction parameter on properties of thermosensitive poly(N-isopropylacrylamide) microspheres prepared by precipitation and dispersion polymerization. Journal of Polymer Science: Part A: Polymer Chemistry, 2006, 44: 968–982
14. Ye Q, Zhang X F, Ge X W, Zhang Z C. Study on radiation-induced dispersion polymerization of vinyl acetate in polar media. Acta Polymerica Sinica, 2003, (5): 718–723 (in Chinese)
15. Terri C, Jeremy L, Joseph M D. Dispersion polymerization of 1-vinyl-2pyrrolidone in supercritical carbon dioxide. Macromolecules, 2000, 33(6): 1917–1920
16. Turner D T, Schwartz A. The glass transition temperature of poly(N-vinylpyrrolidone) by differential scanning calorimetry. Polymer, 1985, 26(5): 757–762