# Synthesis of Monodispersed Polyacrylonitrile Microspheres by Dispersion Polymerization

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**ABSTRACT:** Monodispersed polyacrylonitrile (PAN) microspheres shape have been successfully synthesized by dispersion polymerization in the presence of polyvinylpyrrolidone (PVP) as stabilizer. Transmission Electron Microscopy (TEM) and Particle Size and Distribution Analyzer were used to characterize the morphology and dispersibility of PAN microspheres, respectively. Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) were applied to characterize the structure of PAN. Finally, the crystallinity of PAN microspheres was investigated by X-ray Diffraction (XRD). The results show that PAN microspheres have a regular sphere shape and narrow dispersity with a monodispersity index of 1.17. The crystallization of PAN and the existence of PVP layer affect the morphology of PAN microspheres. The effects of various polymerization factors on the particle size distribution of PAN microspheres have also been studied. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

**Key words:** FTIR; TEM; particle size distribution; polymer synthesis and characterization

## INTRODUCTION

Monodispersed polyacrylonitrile (PAN) microspheres have wide applications in enzyme immobilization,[1] pigments,[2] and excellent precursor as carbon fiber[3] due to their excellent characteristics, such as good chemical stability, oxidation-resistant, solvent-resistant, and easier to react with other reactants.[4] Besides, the polar nitrile group in the acrylonitrile provides a strong intermolecular force between polymer chains, which results in good rigidity of PAN microspheres. Therefore, PAN can meet the requirement of good rigidity for template microspheres. Various methods for manufacturing PAN microspheres have been developed, such as electro spray ionization method,[5] precipitation polymerization,[6] dispersion/emulsion polymerization,[7] carbon dioxide dispersion polymerization,[8] and composite PAN microspheres based on single-step swelling of uniform polystyrene template microspheres.[9] Among these methods, dispersion polymerization is a novel and worthy method to prepare monodispersed microspheres.[10–13] The reaction medium is selected not only for its nonsolvent properties for the forming polymer but also its solubility properties for other reagents. In our former experiments, monodispersed polyacrylamide (PAM) microspheres were prepared by dispersion polymerization with PVP as stabilizer,[14] which had regular shape and narrow dispersity. However, the strength of PAM is poor, so the microsphere would break up at fast mechanical stirring. It is necessary to choose PAN which strength is higher than PAM to prepare template microspheres.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN), Azodiisobutyramidinedihydrochloride (AIBA), and ethanol were purchased from Tianjin Kewei Reagents Company. Polyvinylpyrrolidone (PVP, K30) was purchased from Tianjin Ruijinte Reagents Company. All of the reagents were of analytical reagent grade and were used without further purification.

### Polymerization of PAN microspheres

AN, PVP, and AIBA were subsequently dissolved in ethanol/water mixture (100 g), and then the solution was added into the rotation reactor by a certain speed (Table I). Rotation reactor was composed of round-bottom flask, condenser pipe, water bath, and vacuum pump. Condenser pipe joined with round flask which was heated in water bath at 75°C while

### TABLE I
### Recipe for the Dispersion Polymerization of PAN Microspheres

| Number | AN (wt %) | PVP (wt %) | AIBA (wt %) | Rotation (rpm) | Ethanol/ water ratio, (w/w) |
|---|---|---|---|---|---|
| A1 | 6 | 10 | 0.04 | 110 | 7/3 |
| A2 | 8 | 10 | 0.04 | 110 | 7/3 |
| A3/B3/C1/D6/E4 | 10 | 10 | 0.04 | 110 | 7/3 |
| A4 | 12 | 10 | 0.04 | 110 | 7/3 |
| A5 | 14 | 10 | 0.04 | 110 | 7/3 |
| A6 | 16 | 10 | 0.04 | 110 | 7/3 |
| B1 | 10 | 6 | 0.04 | 110 | 7/3 |
| B2 | 10 | 8 | 0.04 | 110 | 7/3 |
| B4 | 10 | 12 | 0.04 | 110 | 7/3 |
| B5 | 10 | 14 | 0.04 | 110 | 7/3 |
| C2 | 10 | 10 | 0.06 | 110 | 7/3 |
| C3 | 10 | 10 | 0.08 | 110 | 7/3 |
| C4 | 10 | 10 | 0.10 | 110 | 7/3 |
| C5 | 10 | 10 | 0.12 | 110 | 7/3 |
| D1 | 10 | 10 | 0.04 | 110 | 5/5 |
| D2 | 10 | 10 | 0.04 | 110 | 6/4 |
| D3 | 10 | 10 | 0.04 | 110 | 7/3 |
| D4 | 10 | 10 | 0.04 | 110 | 8/2 |
| D5 | 10 | 10 | 0.04 | 110 | 5/1 |
| D7 | 10 | 10 | 0.04 | 110 | 7/1 |
| D8 | 10 | 10 | 0.04 | 110 | 9/1 |
| E1 | 10 | 10 | 0.04 | 70 | 7/3 |
| E2 | 10 | 10 | 0.04 | 90 | 7/3 |
| E3 | 10 | 10 | 0.04 | 100 | 7/3 |
| E5 | 10 | 10 | 0.04 | 130 | 7/3 |
| F1 | 4 | 14 | 0.12 | 70 | 7/3 |
| F2 | 6 | 14 | 0.12 | 70 | 7/3 |
| F3 | 8 | 14 | 0.12 | 70 | 7/3 |

rotation. Through this way the system was heated uniformly and the reaction rate increased. After the polymerization for 6.5 h under 75°C, then the PAN microspheres were redispersed in ethanol under ultrasonication for 30 min after centrifuged at 10,000 rpm. These operations were repeated three times for avoiding the aggregation of microspheres.

### Characterization

Samples used for FTIR, NMR, and XRD experiments were prepared by three steps. First, samples were centrifuged at high speed, and then were dispersed in anhydrous ethanol; finally, the samples were dried in a vacuum drying oven to constant weight.

Morphological observations and size distribution

Transmission electron microscopy (TEM) was adopted to characterize the structure of PAN microspheres. A small amount of samples were diluted with anhydrous ethanol, and then dispersed under the ultrasonic dispersion at room temperature for 0.5 h. TEM was performed on a PHILIPS TECNAI G2 F20 using an accelerating voltage of 80 kV.

The particle size distribution of PAN microspheres was determined by Particle Size and Distribution

Analyzer (HORIBA CAPA-700, Brookhaven). Polydispersity index (PDI) was used to characterize particle size distribution. The particle size distribution of PAN microspheres was narrow, and the monodispersity was better, when the PDI was close to 1.

The polydispersity index (PDI) of PAN microspheres was calculated by the following formulas[12]:

$$D_n = \frac{\sum_{i=1}^{n} d_i}{n} \qquad (1)$$

$$D_w = \frac{\sum_{i=1}^{n} d_i^4}{\sum_{i=1}^{n} d_i^3} \qquad (2)$$

$$\mathrm{PDI} = \frac{D_w}{D_n} \qquad (3)$$

where $D_n$ is the number average diameter, $D_w$ is the weight average diameters, $d_i$ is the diameter of the PAN microspheres, and $n$ is the number of the microspheres.

Fourier transform infrared (FTIR) analysis

The conventional potassium bromide (KBr) method was employed to measure the infrared spectra of the samples. All IR spectra were obtained with the range of 4000–400 cm$^{-1}$ using a Bio-Rad FTS 135 FTIR spectrometer operating at a resolution of 1 cm$^{-1}$.

Nuclear magnetic resonance (NMR) analysis

The NMR spectra were recorded on 13C VARIAN INFINITY PLUS 300 MHz NMR instrument.

*X-ray diffraction (XRD) analysis*

XRD patterns were obtained by X-ray diffractometer (DMAX-RC, Rigaku) with Cu K radiation (=0.15406 nm), in order to determine the changes in crystalline before and after the reaction. Test conditions: CuK radiation (=0.15406 nm), tube voltage (40 Kv), tube electric current (100 mA), scanning speed (4°/min), and scan range from 10° to 90°.

## RESULTS AND DISCUSSION

### Influence of reaction conditions on particle size and size distribution

Five series of experiments (A–E) were carried out to investigate the influence of polymerization conditions on the final average particle size of PAN microspheres.

Figure 1 illustrates the influence of monomer concentration on the average particle size of PAN (A1–A6) microspheres. It shows that the average particle size of PAN microspheres increases firstly at low concentration of monomer AN (A1 to A4, range
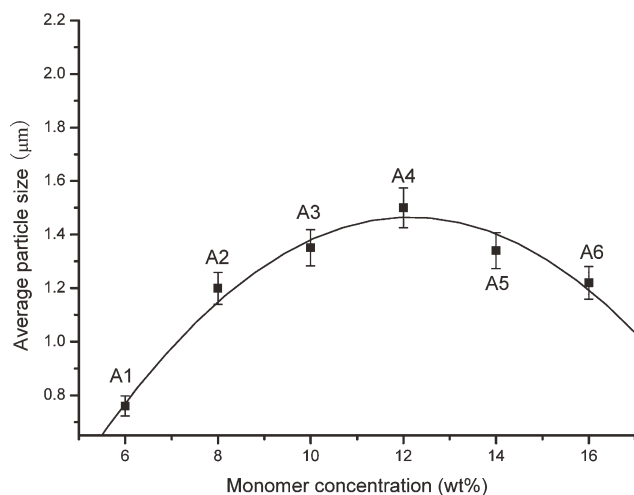
**Figure 1** Influence of monomer concentration on the average size of PAN (A1–A6) microspheres (A1–A6: AN monomer is 6% (A1), 8% (A2), 10% (A3), 12% (A4), 14% (A5), 16% and (A6); PVP concentration is 10%; AIBA concentration is 0.04%; rotation of the rotating reactor is 110 rpm; and ethanol/water ratio is 7/3).

from 6 to 12%) but decreases with the increase of monomer concentration (A4 to A6, range from 12 to 16%). The reason may be that the increase of the monomer concentration causes an increase in the polymerization rate,[15,16] and also improves the solubility of the generated oligomers in the medium,[8] therefore the molecular chain lengths of oligomers could grow longer before separate out. Both effects contribute to the increase in particle size. Figure 2 illustrates the presence of particles [Fig. 2(b)] much smaller than those with low concentration of AN monomers [Fig. 2(a)]. The active radicals in the oligomer chain transfer to the monomer become easier when the monomer concentration reaches to a certain value, this leads to a decrease in the particle size of PAN microspheres.

Figure 3 illustrates the effect of the PVP concentration on the average particle size of the PAN (B1–B5) microspheres. The increase in the concentration of PVP causes the decrease in the average particle size of PAN microspheres (B1 to B5, range from 6 to 14%). The steric effect of PVP contributes to the stability of microspheres, the mechanism is as follows: the stabilizer adsorb on the surface of microspheres and consequently preventing the collision of particles. As a result, the number of stable nuclei increases with the raise concentration of stabilizer, and correspondingly smaller particles were produced.[17,18] In addition, the viscosity of medium increases with the increase of PVP concentration, thereby increases the resistance of particles collision thus PAN microspheres with smaller size are produced. The common effect of both aspects eventually leads to the average particle size of PAN micro-

spheres reducing with the increase of PVP concentration.

Figure 4 depicts the influence of initiator concentration on the average particle size of the PAN (C1–C5) microspheres. The average particle size of PAN microspheres increase with increasing of the initiator concentration (C1 to C5, range from 0.04% to 0.12%). With the increase of initiator concentration, there is an augment in the oligomeric radicals' concentration, so, each molecular chains become shorter which would introduce a better solubility to the oligomer, and the growing microspheres can absorb more oligomeric chains. This may lead to an increase in their size.[19–21] In addition, the probability of the active radicals transfer to stable macromolecules increase with the initiator concentration increasing, and form more activity growth point on the surface of growing microspheres to capture more monomers, this is also an important way to increase the microspheres size.

Figure 5 displays that the average particle size of the PAN depends on the polarity of the reaction medium, which we can alter by adjust ethanol/
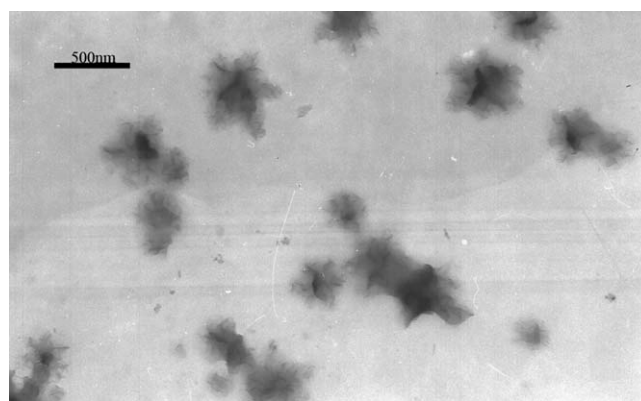


(a)
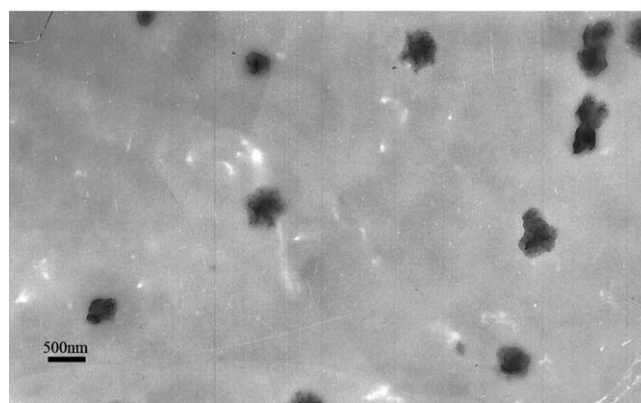


(b)

**Figure 2** TEM images of PAN microspheres prepared by dispersion polymerization (A1: AN monomer is 6% (a, A1) A5: AN monomer is 14% (b, A5); PVP concentration is 10%; AIBA concentration is 0.04%; rotation of the rotating reactor is110 rpm; and ethanol/water ratio is 7/3).
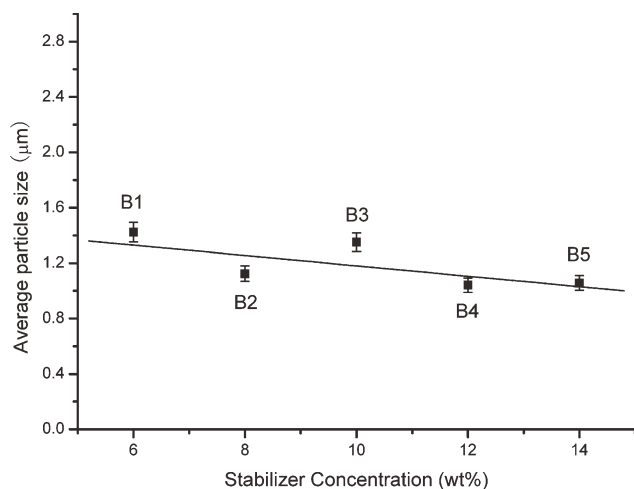
**Figure 3** Influence of stabilizer PVP (B1–B5) concentration on the average size of PAN microspheres (B1–B5: AN monomer is 10%; PVP concentration is 6% (B1), 8% (B2), 10% (B3), 12% (B4), and 14% (B5); AIBA concentration is 0.04%; rotation of the rotating reactor is 110 rpm; and ethanol/water ratio is 7/3).



**Figure 5** Influence of ethanol/water ratio on the average size of PAN (D1–D8) microspheres (D1–D8: AN monomer is 10%; PVP concentration is 10%; AIBA concentration is 0.04%; rotation of the rotating reactor is 110 rpm; and ethanol/water ratio is 5/5(D1), 6/4 (D2), 7/3 (D3), 8/2 (D4), 5/1 (D5), 6/1 (D6), 7/1 (D7), and 9/1 (D8)).

water ratio. At low ethanol/water ratio (PAN-D1 to PAN-D4, range from 5/5 to 8/2), the average particle size of PAN increases, but begin to decrease when the ethanol/water ratio reach 8/2(PAN-D4 to PAN-D8, range from 8/2 to 9/1). The main reason is that the critical oligomer chain length becomes longer and the growing particles can capture longer chains with the increasing amount of ethanol, all of which result in the increase of polymer particle size. On the other hand, cause by the reduction of water in the reaction medium, stabilizer solubility in the reaction medium reduce which weaken the sta-
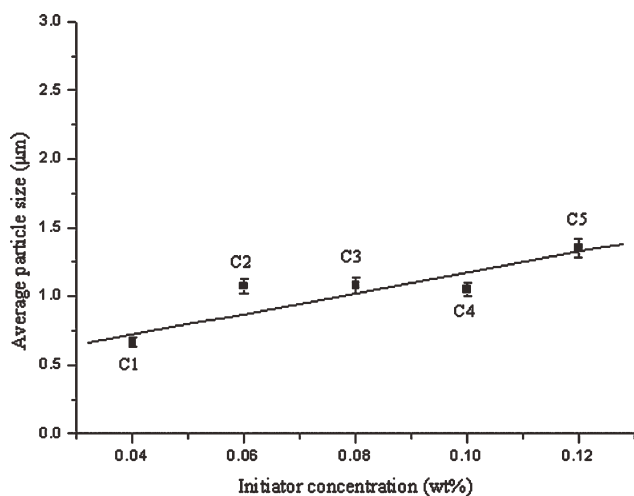
bility of growth nuclear, and all the above induce the possibility of secondary nucleation, so the particle size decrease with further increase of ethanol concentration.

The influence of the speed of rotation on average particle size of the PAN (E1–E5) microspheres is illustrated in Figure 6. The increase in the rotation speed (E1 to E5, range from 70 to 130 rpm) leads to the decrease in the average particle size of PAN. It is possibly because the polymerization system is homogeneous before dispersion polymerization, but the number of nucleation increase with the speed up of rotation in the process of oligomer radical



**Figure 4** Influence of initiator concentration on the average size of PAN (C1–C5) microspheres (C1–C5: AN monomer is 10%; PVP concentration is 10%; AIBA concentration is 0.04% (C1), 0.06% (C2), 0.08% (C3), 0.10% (C4), and 0.12% (C5); rotation of the rotating reactor is 110 rpm; and ethanol/water ratio is 7/3).
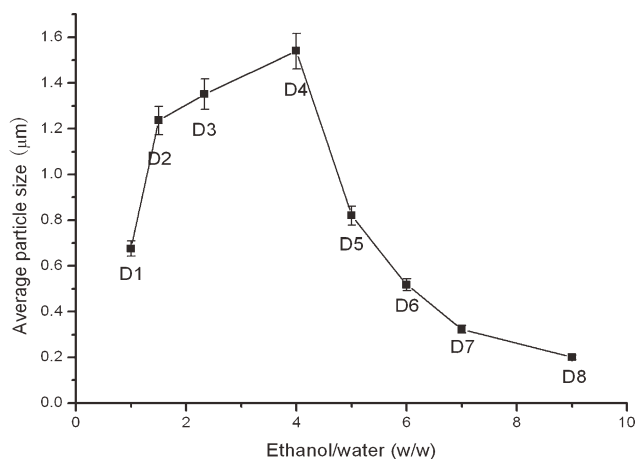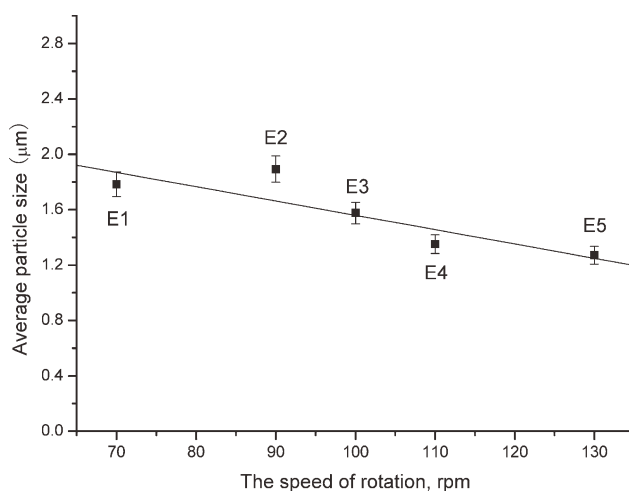


**Figure 6** Influence of the speed of rotation on the average size of PAN microspheres (E1–E5) (E1–E5: AN monomer is 10%; PVP concentration is 10%; AIBA concentration is 0.04%; rotation of the rotating reactor is 70 rpm (E1), 90 rpm (E2), 100 rpm (E3), 110 rpm (E4), and 130 rpm (E5); and ethanol/water ratio is 7/3).
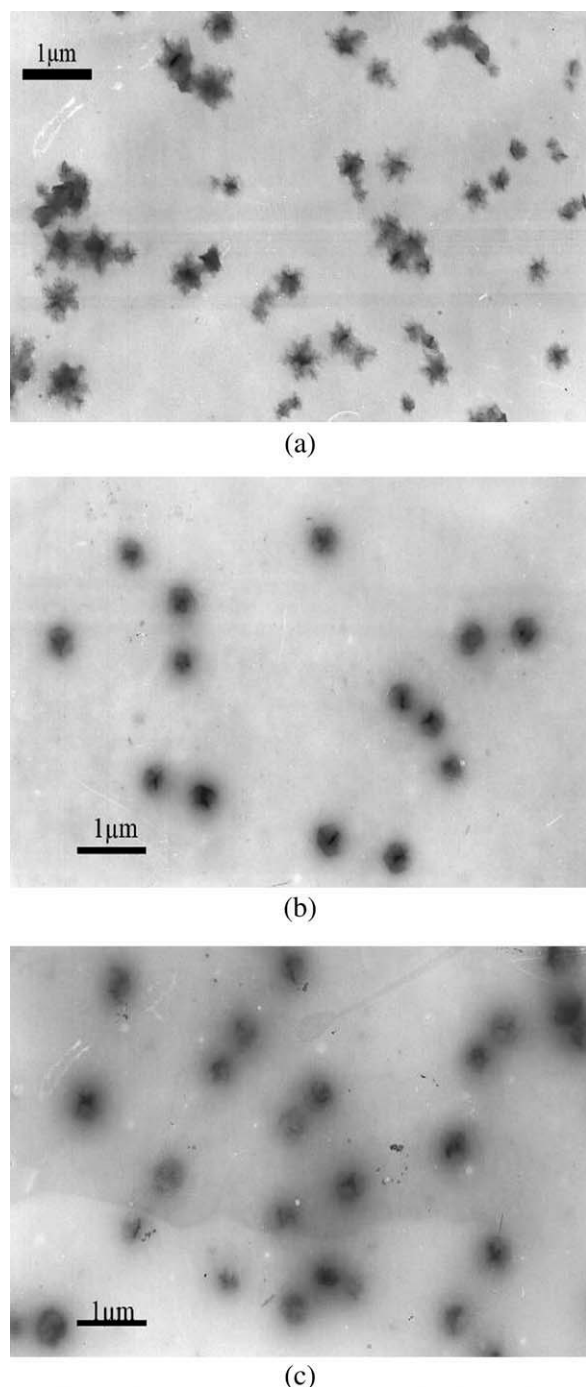
(a)

(b)

(c)

**Figure 7** TEM images of PAN microspheres prepared by dispersion polymerization (F1–F3: AN monomer is 4% (a, F1), 6% (b, F2), and 8% (c, F3); PVP concentration is 14%; AIBA concentration is 0.12%; rotation of the rotating reactor is 70 rpm; and ethanol/water ratio is 7/3).

settlement, meanwhile, the number of particle increase make each PAN microspheres absorb less monomer, which resulted in the decrease of particle size of PAN microspheres with increasing of rotation speed.

According to the analyses above, in order to get the microspheres with maximum particle size, we chose the reaction conditions as it shows in Table I (F1–F3).

## Morphological observations and size distribution

TEM pictures of F1 (AN% = 4), F2 (AN% = 6), and F3 (AN% = 8) microspheres are shown in Figure 7(a), Figure 7(b,c), respectively. As can be seen from Figure 7(a), the F1 microspheres have a poor sphere shape at that monomer concentration, and it is clearly that some branches appear around the microspheres. The F2 microspheres have regular sphere shape and narrow dispersity, which illustrates the condition of F2 is relative fine. Compared with Figure 7(b), the F3 microspheres also display sphere shape but they are less regular than F2. This indicates that the concentration of AN monomer could change the morphology of PAN microspheres. Account for the branches in some PAN microspheres may be that crystallization (see XRD analysis) occurs in the dispersion polymerization process due to the strong polarity of nitrile group.[6,7,22]

At the same time, it is interesting to note that the edge of some PAN microspheres could not be observed clearly. Guha and Mandal[23] also observe this phenomenon, they think there maybe stabilizer layer around microspheres. So, we think the reduction of shear stress in the system causes the aggregation of PVP on the surface of PAN microspheres, therefore PVP layer existence and cause the edge of some PAN microspheres cannot be seen clearly.

Figure 8 displays the particle size distribution of F2 microspheres. It can be observed that over 80% PAN microspheres' size are between 400 and 700 nm and its PDI is 1.17 which is better than those in some previous reports.[7,24] This shows that the
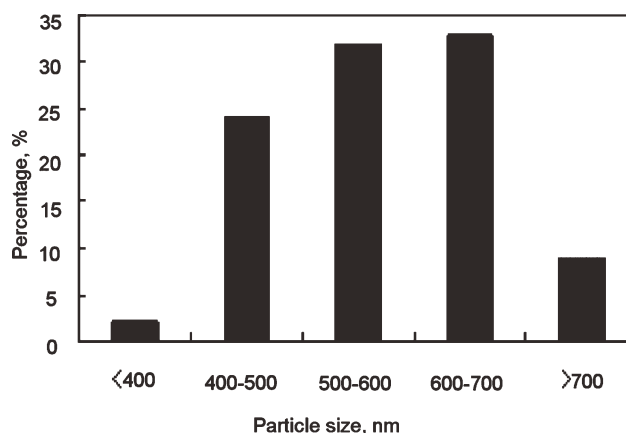


**Figure 8** Histogram of size distribution of PAN-F2 microspheres (F2: the concentration of acrylonitrile monomer is 6%, PVP concentration is 14%, AIBA concentration is 0.12%, rotation of the rotating reactor is 70 rpm, and ethanol/water ratio is 7/3.).
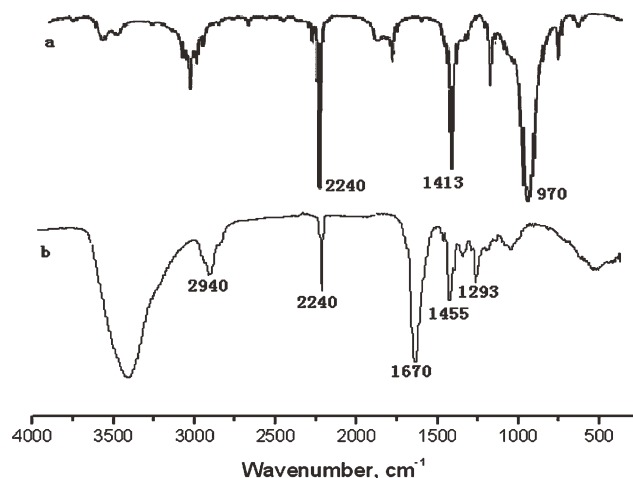
**Figure 9** FTIR spectra of AN monomer (a), PAN-F2 polymer (b) prepared by dispersion polymerization. (F2: the concentration of acrylonitrile monomer is 6%; PVP concentration is 14%; AIBA concentration is 0.12%; rotation of the rotating reactor is 70 rpm; and ethanol/water ratio is 7/3).

rotating reactor make the reaction become more moderate, thus, it is more beneficial to prepare PAN microspheres with regular shape and narrow dispersity by dispersion polymerization.[25]

## FTIR analysis

Figure 9 shows the FTIR spectra of AN monomer and F2 polymer. The peaks at 2940 cm$^{-1}$, 2240 cm$^{-1}$, and 1455 cm$^{-1}$ in Figure 9(b) are nearly the same with those in Figure 9(a), which are assigned to the saturation stretching vibration of carbon hydrogen bond (C—H), the absorption of nitrile groups (—CN), and absorption peak of methylene group (—CH$_2$—), respectively. However, the strongest peak in Figure 9(a) is double bond stretching vibration at 970 cm$^{-1}$, which disappears in Figure 9(b). These prove that AN monomer is polymerized to form PAN microspheres successfully.

In Figure 9(b), newborn bands appear at 1293 cm$^{-1}$ and 1670 cm$^{-1}$ correspond to the tertiary amine groups and carbonyl group in PVP. It indicates that there is remaining PVP in the sample. According to the particle formation proposed by Tseng et al.,[26] PVP molecules were absorbed by aggregates of growing polymer chains and finally anchored on the mature particles, in order to stabilize the dispersion of particles in the polar medium. The anchored PVP resulted from possible adsorbing or grafting could not be washed out. This indicates that there are more than physical equations between PVP and PAN microspheres. It is believed that when the shear stress is greatly reduced in rotating reactor, the stabilizer PVP have more chance to react with the PAN polymer.
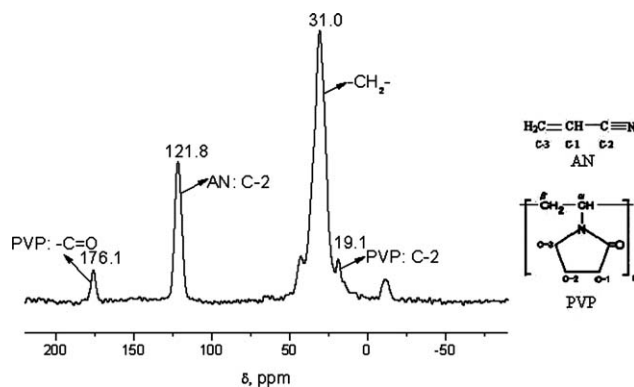
**Figure 10** $^{13}$C NMR spectra of PAN-F2 microspheres. (F2: the concentration of acrylonitrile monomer is 6%; PVP concentration is 14%; AIBA concentration is 0.12%; rotation of the rotating reactor is 70 rpm; and ethanol/water ratio is 7/3).

## NMR analysis

Figure 10 exhibits the NMR analysis of F2 microspheres. The peaks at 121.8 ppm representing the group of —CN and 31.0 ppm corresponds to —CH2—.[15] For the AN monomer, the typical bands are 107 and 137 ppm which represent C-1 and C-3 atom, respectively, cannot be find in Figure 10. Both of these phenomena demonstrate that the AN monomers are polymerized successfully. In addition, two new peaks at 176.1 ppm for carbonyl group and 19.1 ppm for C-2 of PVP indicate that a certain amount of PVP remains on the surface of PAN microspheres and the chemical interaction between PAN and PVP is further proved.

## XRD analysis

Figure 11 shows XRD pattern of F2 microspheres. The crystallinity of the PAN chains in the
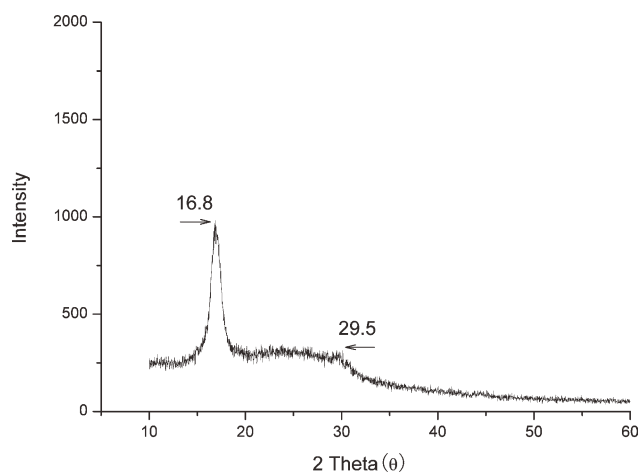


**Figure 11** XRD spectra of PAN-F2 microspheres (F2: the concentration of acrylonitrile monomer is 6%, PVP concentration is 14%, AIBA concentration is 0.12%, rotation of the rotating reactor is 70 rpm, and ethanol/water ratio is 7/3).

microspheres is confirmed by X-ray diffractograms. The following Bragg planes for PAN microspheres are analyzed:[010] and [300], corresponding, respectively, to the diffraction angles $2\theta = 16.8°$ and $29.5°$. According to this data, the crystallinity is about 20%, which is higher than that have been reported.[6,22,24] These XRD results indicate the PAN chains prepared by dispersion polymerization do not precipitate randomly but form crystal structure, which result in the branches appear around the PAN microspheres. This crystalline structure obtains from the special spatial helical conformation of PAN chains due to the strong dipole of the nitrile groups. To get PAN microspheres with good shape, adding comonomer to the system (such as styrene, etc.) may disrupt the crystallization of acrylonitrile copolymer. So, PAN microspheres with good shape could be obtained.[27]

## CONCLUSIONS

Increase the initiator concentration lead to an increase in the average particle size of PAN microspheres. The average particle size of PAN microspheres increase at first and decrease afterward with the increase of monomer concentration and ethanol/water ratio. Average particle size of PAN microspheres decrease with an increase in the stabilizer concentration and the speed of rotation.

PAN microspheres with regular shape and narrow dispersity are synthesized through dispersion polymerization. The particle size of over 80% PAN microspheres (F2) is between 400 and 700 nm with a monodispersity index of 1.17. Due to the reduction in shear stress caused by the utilization of rotary reactor, there is a layer of PVP remaining on the PAN microspheres, and a kind of chemical interactions exist between PVP and PAN according to FTIR and NMR analysis. XRD result proves PAN microspheres have crystal structure with the crystallinity of about 20%, which can also affect the morphology of microspheres.

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