Effects of the Electrospray Ionization Parameters on the Formation and Morphology of Colloidal Microspheres of Polyacrylonitrile

Xiufeng Hao,[1] Xiaofeng Lu,[1] Zhenyu Li,[1] Yiyang Zhao,[1] Tiecun Shang,[1] Qingbiao Yang,[1] Ce Wang,[1] Lijuan Li[2]

[1]*Alan G. MacDiarmid Institute, Jilin University Changchun, 130012, People's Republic of China*
[2]*Department of Chemistry and Biochemistry, California State University Long Beach, Long Beach, California 90840*

Received 6 October 2005; accepted 12 April 2006
DOI 10.1002/app.24731
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyacrylonitrile colloidal microspheres have been successfully prepared with different concentrations of electrospraying polyacrylonitrile solutions. The morphology of the colloidal spheres has two kinds of structures and is strongly affected by electrospray-ionization parameters, such as the polymer concentration, applied voltage, and distance between the electrodes. The solvent can also affect the morphology of polyacrylonitrile. The optimum conditions for preparing colloidal spheres have been found, and differential scanning calorimetry results indicate that polyacrylonitrile colloid spheres are amorphous. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2889–2893, 2006

Key words: colloids; particle size distribution

INTRODUCTION

Monodisperse colloids, especially polymer colloidal spheres with nanometer-to-submicrometer diameters, have been attracting considerable attention for their potential applications in the fields of optics, magnetics, electronics, colloidal chemistry, biochemistry, and medicine.[1–5] Polymer colloids of different chemical compositions can be produced as exceedingly uniform spheres by a process called emulsion polymerization.[6] Recently, a large number of templating methods have been combined with the self-assembly of colloidal spheres.[7–10] Thus, these approaches are usually limited to the formation of colloidal spheres with only some radical polymers, especially polystyrene and poly (methyl methacrylate), and are not applicable to most other common polymers. In this article, we present a simple method called electrospray ionization (ESI) to obtain polymer microspheres. This method is applicable to most common polymers, such as poly(vinyl pyrrolidone), polyacrylonitrile (PAN), and poly(vinyl alcohol). Here we use PAN as an example to demonstrate the effect of ESI parameters on the formation and morphology of colloidal spheres.

Correspondence to: C. Wang (cwang@jlu.edu.cn).
Contract grant sponsor: National 973 Project; contract grant number: 2001CB610500.
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50173009, 50473008, 20320120169.
Contract grant sponsor: DuPont.

The ESI technique was introduced first in 1934 by Formhals,[11] who described an experimental setup for the production of polymer filaments with an electrostatic force. A schematic diagram for interpreting ESI results for polymers is shown in Figure 1. There are basically three components to fulfill the process: a high-voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Talor cone).[12] If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a finely charged jet is ejected. The jet moves toward the metal collecting screen, which acts as a counter electrode. Electrospinning provides an effective way of producing polymer fibers with diameters in the nanometer range.[13–20] ESI has found broad applications in mass spectrometry as a nondestructive method for producing gas-phase ions of biological and synthetic macromolecules. However, there are few reports on the further study of polymer colloid spheres by ESI, although Morozov et al.[21] prepared several polymer ions by ESI. In this article, the effects of the concentrations, solvent, electric field, and tip-to-electrode distance on the morphology of PAN are further studied.

EXPERIMENTAL

Materials and instrumentation

All reagents were used without further purification. PAN (weight-average molecular weight = 80,000)

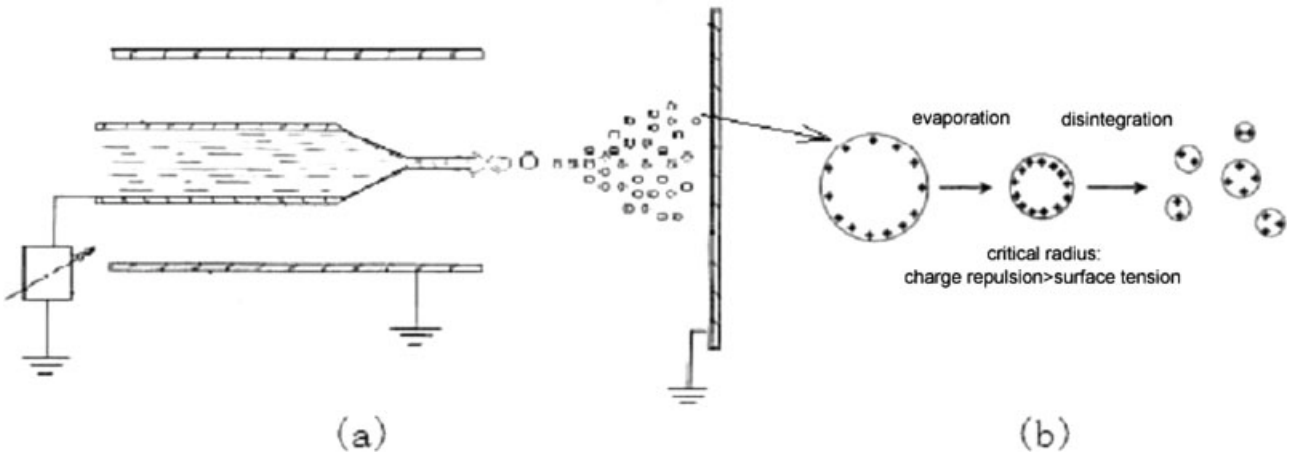

Figure 1 Device for ESI.

was purchased from the Jilin Carbon Group (China). *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) were purchased from Tianjin Tiantai Fine Chemicals Co.

Scanning electron microscopy (SEM) images were recorded on a Shimadzu SSX-550 scanning electron microscope (Japan). Differential scanning calorimetry (DSC) was recorded on a Mettler–Toledo DSC 821e (Switzerland) with a heating rate of 10°C/min from 50 to 400°C.

Preparation of the PAN microspheres

Three series of solutions were prepared for the study: (1) PAN/DMF solutions (1–6 wt %), (2) PAN/DMAc solutions (1–6 wt %), and (3) PAN/DMSO solutions (1–6 wt %). All these solution were stirred for 24 h at room temperature for electrospraying. The PAN solutions were held in a spinning nozzle with a tip diameter of 1 mm, which acted as an anode at a certain distance from the aluminum-foil cathode. A copper grid was stuck on the cathode to collect PAN colloidal microspheres under a certain voltage. The parameters of some samples were adjusted by the distance from the tip to the collector and the voltage.

RESULTS AND DISCUSSION

Effects of the ESI parameters

Concentration

SEM images (Fig. 2) show changes in the morphology of the microstructures with different PAN concentrations. With the decreasing concentration of the PAN/DMF solution, the results are changed from fibers to spheres. That is, the results are in the form of fibers when the PAN concentration is greater than 6 wt %. At 5 wt %, the morphology is changed from fiber to fiber beads, whereas the nanoparticles with a diameter of about 900 nm are generated (maximum = 1.2 μm, minimum = 500 nm) under 4 wt %. At 1 wt % PAN, a half-hollow-sphere structure can be observed under SEM (Fig. 3). A 3 wt % concentration is the best concentration for attaining microspheres with a very round shape and with a narrow diameter distribution in comparison with those at other concentrations (Fig. 4). The lower the concentration is of a system, the higher the surface tension is and the lower the viscosity is.[22] High tension can result in a change from nanofibers to thin fibers with beads to microspheres. The lower the concentration is of the polymer solution, the weaker the entanglement is of the polymer molecules. The formation of the half-hollow spheres may be caused by the collapse of normal spheres. If the proportion of PAN is too low in a sphere, the sphere cannot keep its intrinsic shape and changes into half-hollow spheres.

Distance from the tip to the electrode

Figure 5 presents two SEM images of PAN/DMF colloids with different distances between the capillary tip and the aluminum-foil counter electrode. As the distance increases, the morphology changes from spheres to half-hollow spheres. The solvent begins to evaporate immediately after the jet is formed.[23] The result consists of PAN and DMF. At 10 cm, the evaporation of DMF in the colloids is not excessive, and round spheres are formed, but at 20 cm, the evaporation of DMF is excessive, and the round spheres collapse into half-hollow spheres.

Strength of the electric field

SEM images (Fig. 6) show changes in the morphologies with the strength of the electric field. The results vary as the voltage increases. When the voltage is higher than 2.0 kV, the results comprise beads, fibers, and spheres. The reason is that the jet is unstable under a high voltage, which induces the formation of different products.

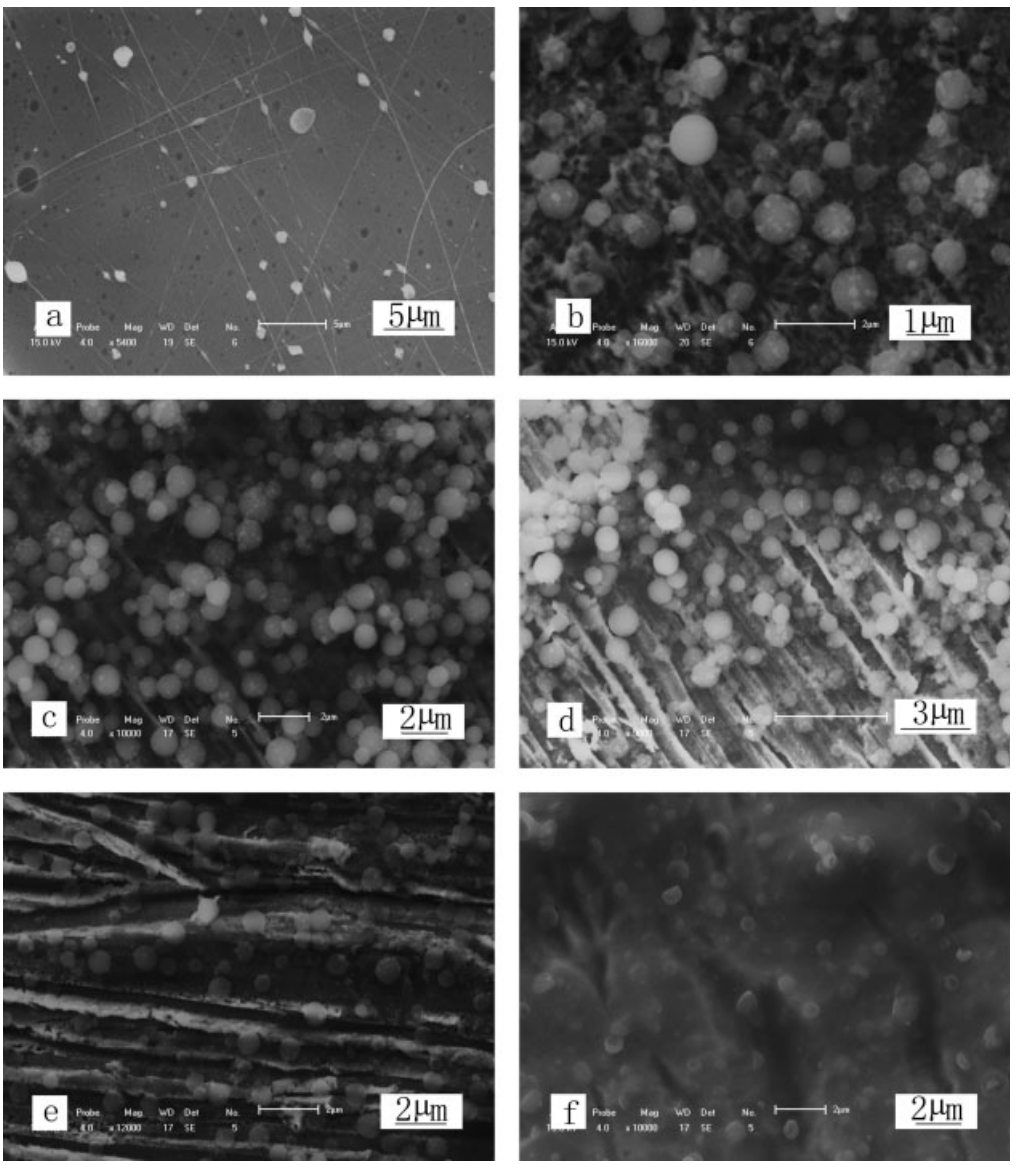

Figure 2 SEM images of PAN/DMF colloids with different concentrations of PAN: (a) 6, (b) 5, (c) 4, (d) 3, (e) 2, and (f) 1 wt %.

Effects of the solvents

Figure 7 shows images of PAN colloids with different solvents. Figure 8 presents statistics for the diameter distribution of PAN/DMAc particles. The morphology and size of the PAN/DMAc colloids are similar to those of PAN/DMF. Therefore, the effect of the solvent is not important for the formation of colloids.

Crystallinity

Evidence for the presence of both amorphous and crystalline regions is present in the DSC results for electrospraying PAN/DMF microspheres. The crystalline peak and melt peak have not been observed (Fig. 9), and this indicates that the PAN/DMF microspheres are perhaps amorphous.

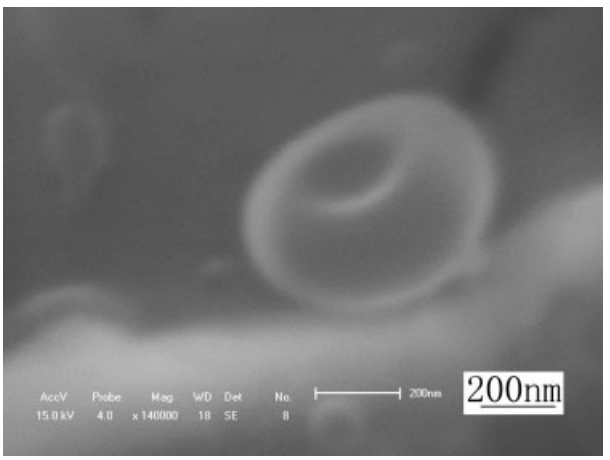

Figure 3 SEM image of PAN/DMF half-hollow colloids at 1 wt %.

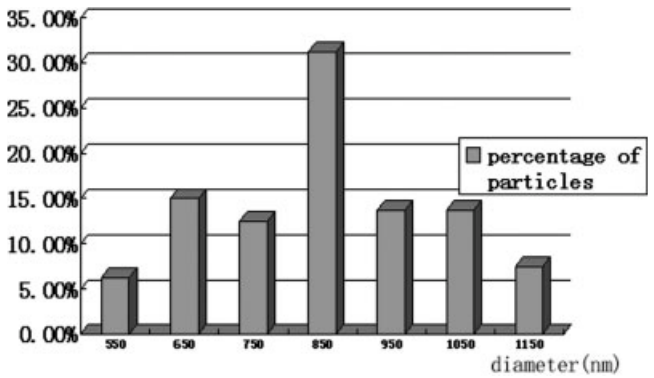

Figure 4 Statistics of the diameter distribution of PAN/DMF particles.

CONCLUSIONS

Electrospraying PAN microspheres have been successfully prepared with different concentrations of electrospraying PAN solutions. The morphology of the microspheres is strongly affected by parameters such as the polymer concentration, applied voltage, and distance between the electrodes. In PAN/DMF solutions, above 6 wt %, fibers form because of the high viscosity; at 2–4 wt %, the expected microspheres form. Half-hollow spheres have been observed

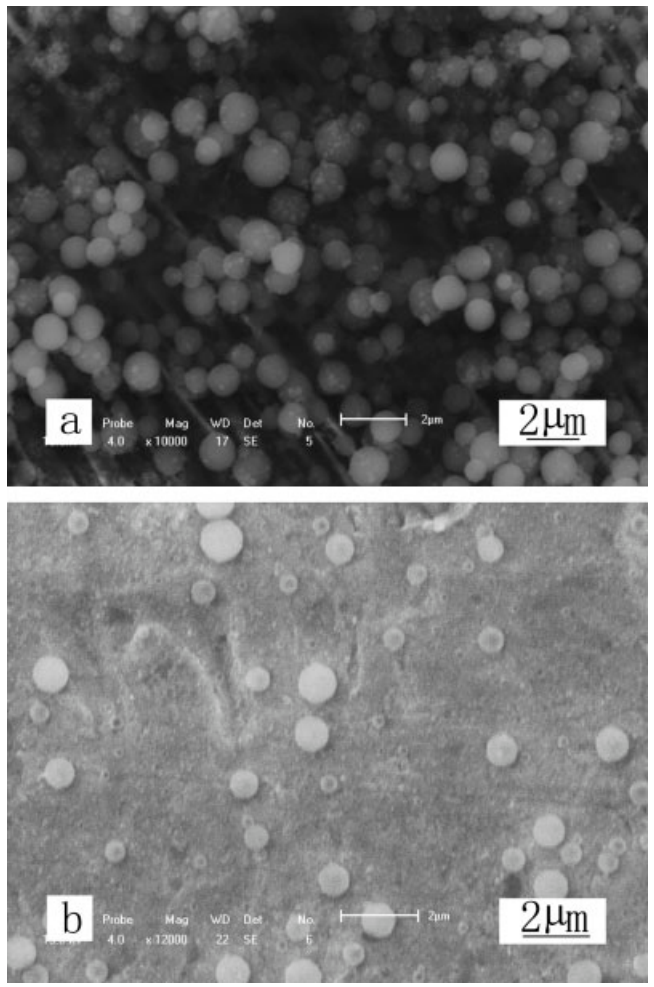

Figure 5 SEM images of PAN colloids with different distances from the tip to the collector: (a) 10 and (b) 20 cm.

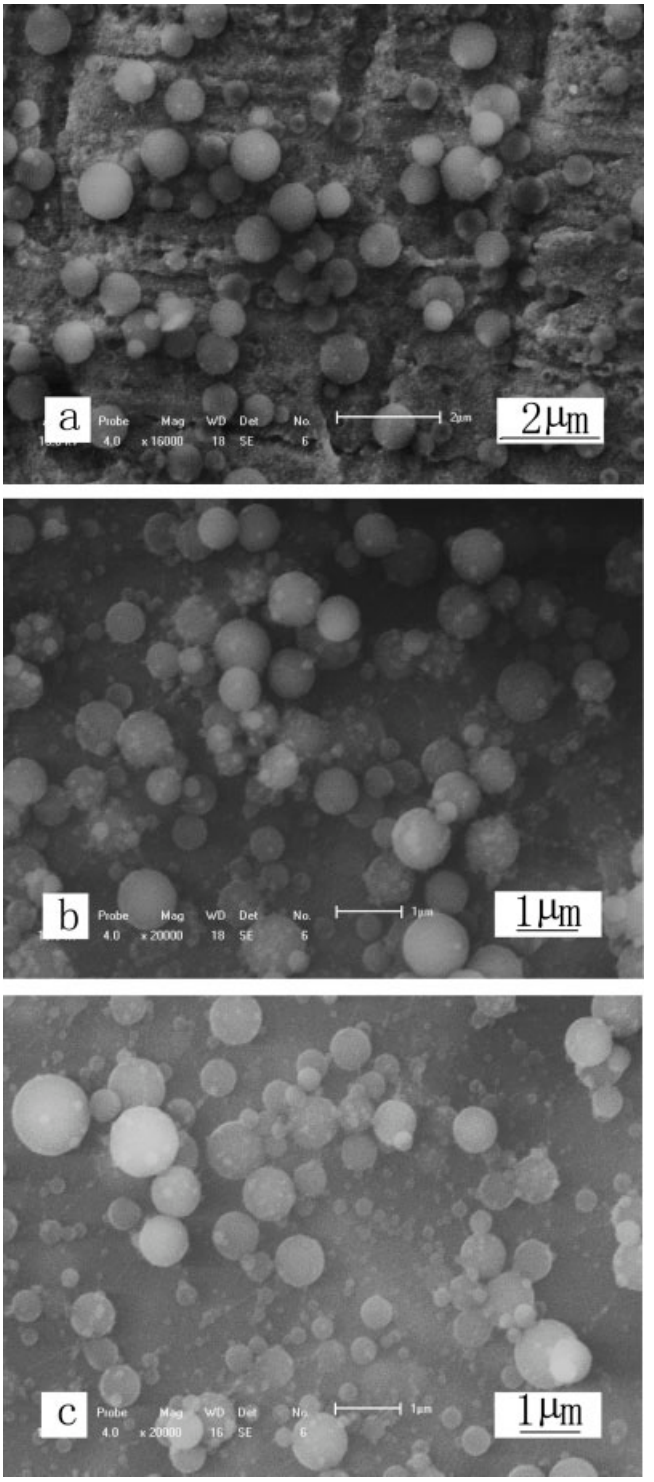

Figure 6 SEM images of PAN results with electric fields of different strengths: (a) 1.4, (b) 1.7, and (c) 2.0 kV.

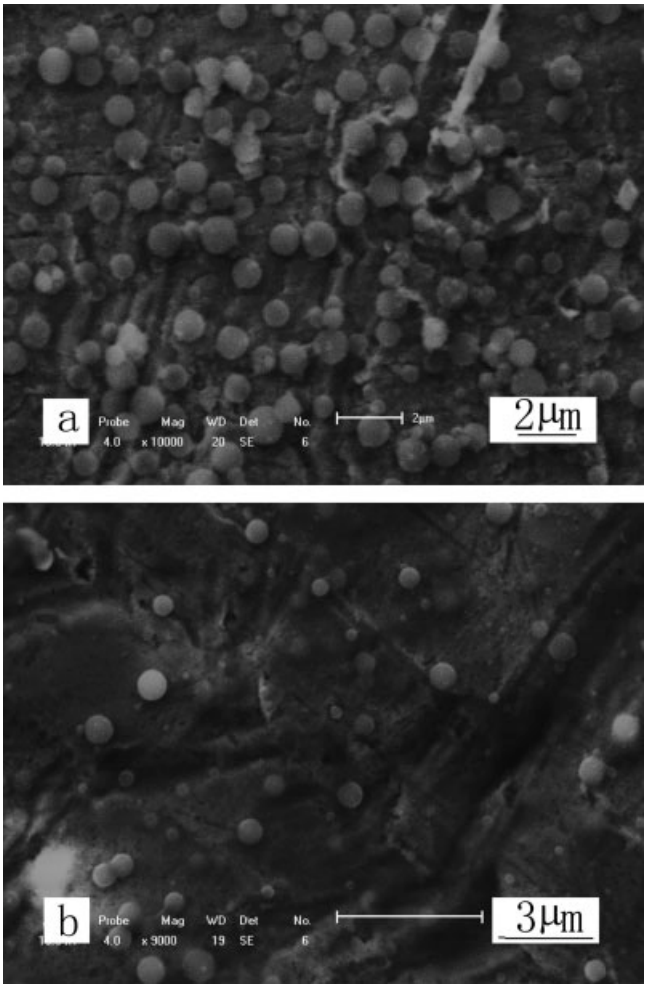

Figure 7 SEM images of PAN colloids in different solvents: (a) 3 wt % PAN in DMAc and (b) 3 wt % PAN in DMSO.

at 1 wt %. Similarly, this can be observed at long distances or high applied voltages, too. The shape of the spheres is not influenced significantly by the species of the solvent. A 3 wt % concentration, 10 cm from the tip to the collector, and 1.1 kV of applied voltage are the optimum conditions for preparing

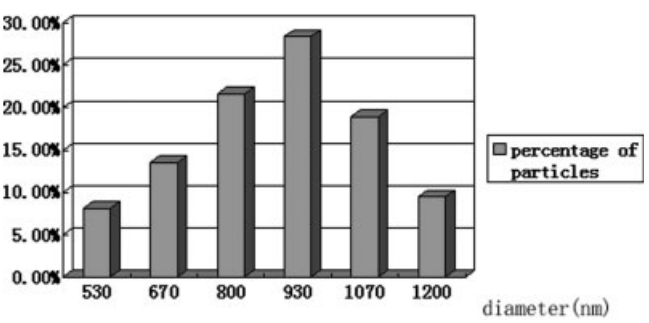

Figure 8 Statistics of the diameter distribution of PAN/DMAc particles.

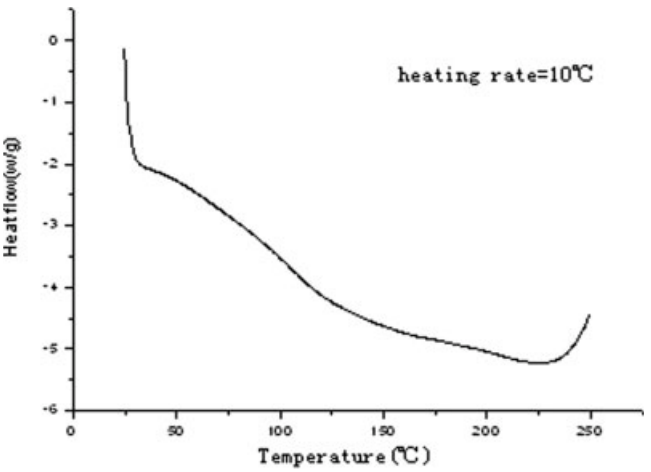

Figure 9 DSC results for electrospraying PAN particles.

microspheres. DSC results indicate that the PAN microspheres are amorphous.

References

1. Jiang, P.; Bertone, J. F.; Colvin, V. L. Science 2001, 291, 453.
2. Xia, Y. N.; Gates, B.; Yin, Y.; Lu, Y. Adv Mater 2000, 12, 693.
3. Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. J Am Chem Soc 1999, 121, 7957.
4. Kondo, Y.; Takayanagi, K. Science 2000, 289, 604.
5. Xia, Y. N. Adv Mater 2001, 13, 369.
6. (a) Emulsion Polymerization; Piirma, I., Ed.; Academic: New York, 1982; (b) Science and Technology of Polymer Colloids; Poehlein, G. W.; Ottewill, R. H.; Goodwin, J. W., Eds.; Martinus Nijhoff: Boston, 1983; Vol. 2.
7. Velev, O. D.; Furusawa, K.; Nagayama, K. Langmuir 1996, 12, 2374.
8. Velev, O. D.; Lenholl, A. M.; Kaler, E. W. Science 2000, 287, 2240.
9. van Blaaderen, A.; Ruel, R.; Wiltzius, P. Nature 1997, 385, 321.
10. Yang, S. M.; Ozin, G. A. Chem Commun 2000, 2507.
11. Formhals, A. U.S. Pat. 1,975,504 (1934).
12. Taylor, G. I. Proc R Soc London Ser A 1969, 313, 453.
13. Senecal, K.; Ziegler, D.; Mosurkal, J.; He, R.; Schreuder-Gibson, H.; Samuelson, L. In Proceedings of the MRS Fall 2001 Meeting; Moss, S. C., Ed.; Vol. 708, Paper BB9.5; 2001.
14. Tsai, P. P.; Schreuder-Gibson, H.; Gibson, P. J Electrost 2002, 54, 333.
15. Wang, X.; Lee, S. H.; Drew, C.; Kumar, J.; Senecal, K. J.; Samuelson, L. In Proceedings of the MRS Fall 2001 Meeting; Moss, S. C., Ed.; Vol. 708, Paper BB10.44; 2001.
16. Zong, X.; Kim, K. S.; Fang, D.; Ran, S.; Hsiao, B. S.; Chu, B. Polymer 2002, 43, 4403.
17. Burgshoef, M. M.; Vancso, G. J. Adv Mater 1999, 11, 1362.
18. Buchko, C. J.; Chen, J. C.; Shen, Y.; Martin, D. C. Polymer 1999, 40, 7397.
19. Gibson, P.; Schreuder-Gibson, H.; Rivin, D. Physicochem Eng Aspects 2001, 469, 187.
20. Kim, K.; Chen, W.; Zhong, M.; Yu, S.; Fang, D.; Hsiao, B.; Chu, B.; Hadjiargyrou, M. In Proceedings of the MRS Fall 2001 Meeting; Moss, S. C., Ed.; Vol. 711, Paper GG4.5; 2001.
21. Morozov, V. N.; Morozova, T. Y.; Kallenbach, N. R. Int J Mass Spectrom 1998, 178, 143.
22. Fong, H.; Chun, I.; Renecker, D. H. Polymer 1999, 40, 4585.
23. Bognizki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A. Adv Mater 2001, 13, 70.