

Self-assembly of Poly(aniline-co-anthranilic acid) Copolymers and PVP into Fibers and Other Microstructures

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The morphology of the self-assembly of poly(aniline-co-anthranilic acid) copolymers (PAAA) and poly(*N*-vinylpyrrolidone) (PVP) into particles in DMF/H₂O solution and fibers in sodium hydroxide solution was studied. Not only the solvent but also the content of PVP affected the morphology significantly. When the content of PVP is zero, no fibers were formed. With the increasing of the content of PVP, more and more fiber junctions appeared.

Synthesis of nanotubes and other nanostructures of conducting polymers has recently generated a great deal of interest because of their unique properties as molecular wires and molecular devices.¹ Among the conducting polymers, polyaniline is an excellent candidate for molecular wires because of its high conductivity, good environmental stability, and convenience of synthesis.^{2,3} Different morphologies of polyaniline have been obtained by changing the synthetic method. Polyaniline particles with needlelike or spherical shapes, for instance, could be obtained by dispersion polymerization in the presence of polymeric stabilizers.^{4,5} Nanotubes or -fibers of polyaniline have been synthesized by using a porous membrane template⁶ or template-free methods.⁷ And microporous polyaniline has been fabricated by using the ordered colloidal assemblies as a template.⁸ Hollow microspheres of polyaniline were also synthesized recently.⁹ But most polyaniline particles and tubes are all formed in the process of oxidation of aniline. Then how to make synthesized polyaniline into different morphologies through changing conditions such as blending with the other organic molecules or polymers has been considerable attention for its facile synthesis.¹⁰ In many cases, the weak interactions such as π - π^* interactions, hydrogen bonds, ionic bonds are driving forces to fabricate different morphologies of conducting polymers.^{11,12} Such interactions of polyaniline with the other polymers will change in different environments which suggested to us that it may be possible to change these environmental factors to self-assemble polyaniline into different morphologies. Here, we report the self-assembly of PAAA and PVP into particles and fibers in different environments. In DMF/H₂O (7:3) solution, PAAA and PVP assembled into microparticles. While they assembled into fibers in 0.1 mol/L sodium hydroxide solutions (Figure 1). In a typical synthesis, PAAA was prepared with Diaz's method.¹³ The self-assembly of PAAA and PVP was prepared by mixing PVP and PAAA in DMF/H₂O (7:3) solution or 0.1 mol/L sodium hydroxide solution. The concentration of PAAA and PVP was both 0.5 mg/mL. The prepared solution was dropped on a clear silicon wafer substrate in order that the solvent dried in air slowly and naturally.

The SEM micrograph of the self-assembly of PAAA and

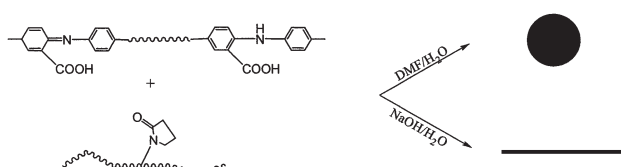


Figure 1. Simplified schematic representation of the self-assembly of poly(aniline-co-anthranilic acid) copolymers and PVP in different solutions.

PVP prepared in DMF/H₂O (7:3) solution is shown in Figure 2. PAAA and PVP particles were obtained in which the particle size was evaluated as 0.8–5.0 μm . However, no polyaniline microparticles were observed when PAAA was replaced by PANI. So it is presumed that the weak interactions such as π - π^* interactions just like the self-assembling of oligothiophene-COOH-coated magnetic nanoparticles into spherical aggregates¹¹ and hydrogen bond between carbonyl and carboxyl or imine groups play an important role in the self-assembly process.

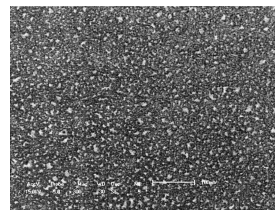


Figure 2. SEM photograph of the self-assembly aggregates of PAAA and PVP prepared in DMF/H₂O solution. Conditions: PAAA = 0.5 mg/mL; PVP = 0.5 mg/mL.

The SEM micrographs of the self-assemblies of PAAA and PVP in 0.1 mol/L sodium hydroxide solution are shown in Figure 3. PAAA and PVP fibers were obtained whose diameter was evaluated as 1.0–5.0 μm . The concentration of sodium hydroxide solution affects the self-assembled structures. When the concentration of sodium hydroxide was from 0.1 to 0.05 mol/L, the morphology of the self-assemblies of PAAA and PVP did not change much. But when the concentration of sodium hydroxide was lower than 0.02 mol/L, fibers were not observed any longer. We also studied the effect of the content of PVP on the morphology. From Figures 3a–3c, we found that, with the increasing of the content of PVP, the diameter and morphology did not change much. And among the fibers much more junctions were observed especially in high content of PVP. Two fibers are often linked together to form Y-junctions, and these can, in turn, construct more complicated junctions. When the concentration of PVP is zero, no fibers were observed (Figure 3d). So we can see that the concentration of PVP plays an impor-

tant role on the morphology of the self-assemblies. Compared with the two polymers in DMF/H₂O (7:3) solutions, the carboxyl group of PAAA disappeared because of the ionization in the sodium hydroxide solution. And the main interactions between the PAAA and itself were possibly ionic bond interactions. The ionic bonds and the other interactions such as hydrogen bonds and π - π^* interactions between PAAA and PVP make the fibers formed together.

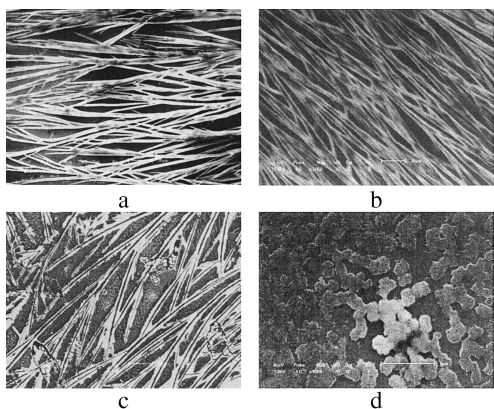


Figure 3. SEM photographs of the self-assembly aggregates of PAAA and PVP prepared in sodium hydroxide solution: $[\text{OH}^-] = 0.1 \text{ mol/L}$, $[\text{PAAA}] = 0.5 \text{ mg/mL}$, (a) $[\text{PVP}] = 1.0 \text{ mg/mL}$; (b) $[\text{PVP}] = 0.5 \text{ mg/mL}$, (c) $[\text{PVP}] = 0.25 \text{ mg/mL}$, [d] $[\text{PVP}] = 0$.

The molecular structure of the resulting self-assemblies was characterized by Fourier-transform infrared (FTIR) spectroscopy. In order to reduce the effect of solvent, a minimum solution of the self-assemblies was dropped on fluorite substrate and the sample was treated in air and then under vacuum at room temperature for one day, respectively. For PVP itself, a band at 1654 cm^{-1} assigned as C=O stretching vibration and another band at 1284 cm^{-1} assigned as C-N stretching vibration were observed. It was found that FTIR spectrum of PAAA, for instance, bands of 1654 and 1140 cm^{-1} assigned as C=O and C=N stretching vibration, respectively, were identical to that of PAAA synthesized by a common method.¹³ The characteristic bands of both PAAA and PVP were observed in the self-assembled structures. However, The bands at 1654 cm^{-1} corresponding to C=O stretching vibration in PAAA and PVP turned into 1660 cm^{-1} in DMF/H₂O solution and 1663 cm^{-1} in sodium hydroxide solution. The band at 1140 cm^{-1} (C=N) in PANI was replaced by 1094 cm^{-1} in DMF/H₂O solution and 1106 cm^{-1} in sodium hydroxide solution. Both of the facts indicate that

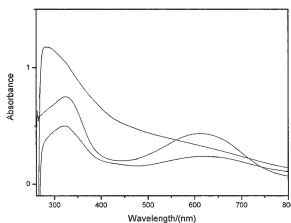


Figure 4. UV-vis spectrum of (a) PAAA, (b) Self-assembly aggregates of PAAA and PVP in DMF/H₂O solution, (c) Self-assembly aggregates of PAAA and PVP in sodium hydroxide solution.

there are some interactions in the self-assembled structure between PAAA and PVP.

UV-vis spectrum was used to study the self-assembly of the PAAA and PVP in DMF solution (Figure 4.). Pure PAAA exhibits two absorptions at 320 and 610 nm. We know that the first peak was ascribed to the π - π^* transition in the benzenoid ring.^{14,15} The second peak is associated with a benzenoid to quinoid excitonic transition.¹⁶ Then we found that the self-assembly of PAAA and PVP in DMF/H₂O solution has the similar result to the PAAA in the UV-vis spectrum at 321 and 611 nm which indicates that the PAAA backbone structure does not change much. However, the C=N stretching vibration peak in PAAA shifted from 1140 to 1094 cm^{-1} from FTIR spectrum. The result probably indicates that the weak interactions change the electronic state of PAAA which showed in FTIR. While UV-vis spectrum did not change much unless the C=N structure change into C-N⁺ after doping with strong acid.¹⁷ In sodium hydroxide solution, the second peak disappeared probably due to the effect of the ionization of carboxyl group and alkali solution to PAAA.

In conclusion, PAAA particles and fibers can be produced by introducing PVP through weak interactions such as π - π^* interactions, hydrogen bonds, and ionic bonds. In DMF/H₂O (7:3) solution, PAAA and PVP assembled into microparticles. While they assembled into fibers in 0.1 mol/L sodium hydroxide solutions. The concentration of sodium hydroxide solutions and the concentration of PVP affect the shape of PAAA fibers significantly.

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References

- 1 Y. Long, Z. Chen, N. Wang, Y. Ma, Z. Zhang, L. Zhang, and M. Wan, *Appl. Phys. Lett.*, **83**, 1863 (2003).
- 2 M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, *Science*, **252**, 1412 (1991).
- 3 Y. N. Xia, J. M. Wiesinger, A. G. Macdiarmid, and A. J. Epstein, *Chem. Mater.*, **7**, 443 (1995).
- 4 B. Vincent and J. Waterson, *Chem. Commun.*, **1990**, 683.
- 5 J. Stejskal, P. Kratochvil, S. P. Armes, S. F. Lascelles, A. Riede, M. Helmstedt, J. Prokes, and I. Krivka, *Macromolecules*, **29**, 6814 (1996).
- 6 C. R. Martin, *Science*, **266**, 1961 (1994).
- 7 H. Oiu, M. Wan, B. Matthews, and L. Dai, *Macromolecules*, **34**, 675 (2001).
- 8 D. Wang and F. Caruso, *Adv. Mater.*, **13**, 350 (2002).
- 9 Z. Wei and M. Wan, *Adv. Mater.*, **14**, 1314 (2002).
- 10 C. He, Y. Tan, and Y. Li, *J. Appl. Polym. Sci.*, **87**, 1537 (2003).
- 11 J. Jin, T. Iyoda, C. Cao, Y. Song, L. Jiang, T. Li, and D. Zhu, *Angew. Chem., Int. Ed.*, **40**, 2135 (2001).
- 12 H. Kosonen, J. Ruokolainen, M. Knaapila, M. Torkkeli, K. Jokela, R. Serimaa, G. Brinke, W. Bras, A. P. Monkman, and O. Ikkala, *Macromolecules*, **33**, 8671 (2000).
- 13 M. T. Nguyen and A. F. Diaz, *Macromolecules*, **28**, 3411 (1995).
- 14 E. Conwell, C. B. Duke, A. Paton, and S. Leyadev, *J. Chem. Phys.*, **88**, 3955 (1988).
- 15 J. Honzl and M. Tlustakova, *Tetrahedron*, **25**, 3641 (1969).
- 16 Y. Furudawa, F. Ueda, Y. Hyodo, and I. Harada, *Macromolecules*, **21**, 1297 (1988).
- 17 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, **65**, 103 (1994).