

Preparation of Electrically Conducting Polypyrrole in Oil/Water Microemulsion

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ABSTRACT: Nanoscopic conducting polypyrrole powder was prepared in an oil/water microemulsion with FeCl_3 as a dopant. Compared with solution and conventional emulsion polymerizations, a microemulsion polymerization system increases the yield of the resultant polypyrrole. The results of FTIR spectra and thermal analysis studies indicate that the microemulsion polymerization system increased the extent of the π -conjugation length along the polymer backbone and ordered the arrangement of the macromolecule chains. These two effects bring about enhanced conductivity as well as higher thermal stability of polypyrrole. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 135–140, 2000

Key words: polypyrrole; microemulsion polymerization; characterization; conductivity; thermal stability

INTRODUCTION

During the past two decades, a wide variety of electrically conducting polymers have been extensively studied due to their exclusive physical properties. Of all these polymers, conducting polypyrrole (PPy) is one of the most promising candidates for its high electrical conductivity and good environmental stability.^{1–4} Usually, PPy can be easily synthesized from a monomer by either the electrochemical method in the form of films or the chemical method to yield powder. Among the studies reported, many scientific works focused on the electropolymerization of pyrrole, and the effects of synthesis conditions have received considerable attention.^{5,6} However, chemical polymerization of pyrrole is also particularly important since the synthesis is a more feasible route for the production of PPy on a large scale. Normally, pyrrole is chemically polymer-

ized in aqueous media in which an oxidative agent is added, and then the black polymer powder “pyrrole black” can be obtained. The chemical synthesis of conducting PPy in aqueous media has been reported in a series of previous works.^{7–9}

Recently, the preparation of nanostructured conducting materials has become an important branch of material research; those materials are expected to exhibit unusual chemical and physical properties and with a view of applications in the biomedical field and microelectronics and information industry areas.¹⁰ Several groups have described the preparation of nanoscopic PPy and polyaniline colloidal particles in aqueous media with a dispersion technique.^{11–13} The disperse agents used were mainly water-soluble polymeric surfactants such as polyvinylpyrrolidone and poly(vinyl alcohol), but the method sometimes resulted in macroscopic precipitation and, in certain cases, a low yield of colloidal particles. To avoid precipitation, Armes et al.¹⁴ prepared colloidal particles by grafting the monomer onto a polymeric surfactant; namely, in the polymerization system, the polymeric surfactant acted not only

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as a steric stabilizer but also as a comonomer, and the nanoscopic microspheres that they obtained were often copolymers or conducting composites.

It is well known that microemulsion polymerization is very effective in producing polymer particles in the size range of 5–100 nm. Microemulsion is an organized microheterogeneous system which provides a large interfacial area and is generally less viscous. Usually, a typical microemulsion system contains water, oil, and a surfactant, often with a cosurfactant to stabilize the system. During the past two decades, many studies have been done on nonconducting polymers,^{15–17} but relatively little work has been conducted on conducting polymers and some of the results reported were conflicting.^{18,19} It was shown recently in Roy and Devi's and our previous works that the orientation behavior of surfactants can be detected in a microemulsion system in which the monomer chains are aligned.^{20,21} More recently, Webber²² also reported the self-assembling behavior of polymers in a microemulsion polymerization system. According to the previous works, it has been widely accepted that microemulsion is a molecularly ordered system.

Based on the previous works, we report here a method of preparation of PPy in a microemulsion system, in which the polymerization of pyrrole is expected to proceed in a molecularly ordered system and pure nanoscopic conducting PPy can be prepared. In this work, FeCl₃ is used as oxidizing agent and sodium dodecylbenzenesulfonic acid (SDBA) and butanol are used as the surfactant and the cosurfactant, respectively.

EXPERIMENTAL

Materials

The pyrrole monomer was freshly distilled under nitrogen pressure before use. FeCl₃, SDBA, butanol, and hexane were all AR grade. The deionized and triply distilled water used throughout the work was deprived of oxygen under a stream of nitrogen.

Synthesis

A microemulsion system was prepared as follows: As an oxidizing agent, 0.49 g FeCl₃ was dissolved in 10 mL distilled water; then, 4 g SDBA, 0.9 mL butanol, and 6 mL hexane were introduced into the FeCl₃ aqueous media. The mixture was

stirred with a magnetic stirrer and the system become transparent suddenly; thus, a clear and transparent microemulsion system was obtained. On stirring, 55 μ L of the pyrrole monomer was added into the prepared microemulsion system, and in the polymerization system, the molar ratio of FeCl₃ to the pyrrole monomer was kept at 3.75. Without more stirring, the polymerization was carried out for 24 h at room temperature. During the polymerization, the color of the system changed from brown–black to black slowly and no evident precipitation was observed. The microemulsion polymerization was terminated by pouring the system into acetone, causing the PPy to precipitate. The black powder was filtered and washed with distilled water and acetone until the SDBA was removed thoroughly. Then, the PPy powder was dried in a vacuum for 48 h at room temperature.

In a similar manner, a conventional emulsion polymerization was taken on with 10% (wt %) SDBA in the FeCl₃ solution; the ratio of oxidant to monomer was kept the same as that in the microemulsion. During the polymerization, the color of the system changed to black quickly, and the polymerization was kept for 24 h at room temperature with vigorous stirring; then, the resultant PPy powder was also rinsed with distilled water and acetone thoroughly and dried in a dynamic vacuum for 48 h at room temperature.

With the same molar ratio of oxidant to monomer, a homogeneous solution polymerization was also carried out for comparison. The solution polymerization was stirred for 24 h at room temperature, and then the obtained PPy was also washed with distilled water thoroughly and dried in vacuum for 48 h at room temperature.

Characterization

Fourier transform infrared (FTIR) spectra of the polymers in KBr pellets were recorded on a Bruker IFS66V spectrometer under a vacuum. The spectra were collected from 4000 to 400 cm⁻¹ with a 4 cm⁻¹ resolution over 50 scans. Thermal analysis (TGA–DTA) of the polymers was carried out on a TA Instruments 2100 thermal analyzer with a heating rate of 20°C min⁻¹ and a dynamic dry air flow of 100 cm³ min⁻¹. The particle size of the polymer latexes were determined by transmission electron microscopy (TEM) and the samples were prepared by placing a drop of diluted latex on a carbon-coated copper grid and placed in the cold stage of a Phillips 300 transmission electron microscope.

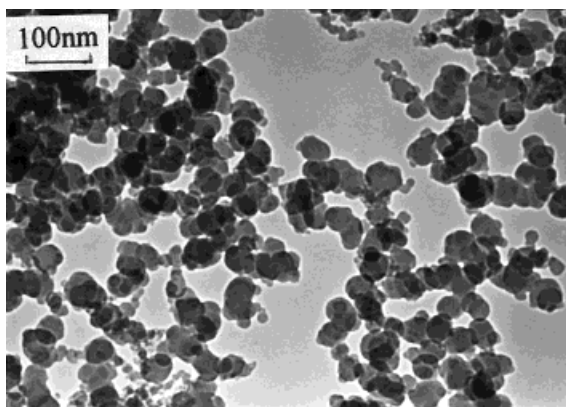


Figure 1 TEM micrograph of PPy particles obtained from the microemulsion system.

RESULTS AND DISCUSSION

The PPy prepared in the microemulsion polymerization was studied by TEM. As shown in Figure 1, the size of the PPy spherical particle is in the range of about 30–50 nm, which confirmed the efficiency of the synthesis of fine polymer particles in the microemulsion system.

Table I shows the elemental compositions, the yields, and the conductivities of the PPy samples prepared from various polymerization conditions. It can be seen that in the PPy's the dopant anions are all FeCl_4^- , and the doping levels of three PPy's are found to be same. This result indicates that the doping level of PPy is dependent mainly on the ratio of the oxidant to the monomer; however, it is little affected by the different polymerization conditions.

The value of the polymerization yields shows that the yield of the PPy powder prepared in the microemulsion system is considerably larger than that obtained from a homogeneous solution and emulsion polymerization systems. According to the results of the elemental analysis, it can be

concluded here that the increase in yield cannot be ascribed to the different contents of the FeCl_4^- anion in the PPy's. This significant difference is probably due to the different particle nucleation processes in the three polymerization systems. In microemulsion polymerization, the nucleation occurs in emulsified monomer droplets and the nucleation process continues throughout the polymerization, while in the homogeneous solution and emulsion polymerization systems, the principal loci are mainly monomer droplets and the particle nucleation process lasts up to less than 10% conversion.^{23,24} The longer the particle nucleation process lasts, the higher the conversion of the polymerization results.

Furthermore, the conductivities of the PPy's obtained from the solution polymerization and emulsion polymerization are also lower than those synthesized in the microemulsion. It has been determined that the macroscopic conductivity of doped conducting polymers depends on the doping level, the charge transport along the polymer chain (intrachain transport), and the charge hopping from polymer chain to polymer chain (interchain transport). At a higher doping level, a longer conjugation length and the ordered arrangement of the macromolecule chains favor the higher conductivity.^{25–27} In this work, the doping levels of the three samples are almost same, and it can be assumed here that the relatively higher conductivity of the PPy synthesized in the microemulsion system may come from the effects of a longer conjugation length and the ordered arrangement of the macromolecule chains.

Information about the structure of PPy was obtained from the FTIR spectra. In Figure 2, similar bands, characteristic peaks of PPy obtained from the chemical polymerization, are observed from 1700 to 800 cm^{-1} , indicating that the main components of each specimen have the same chemical structures. It has been reported that the

Table I Comparison of Elemental Compositions, Yields, and Conductivities of PPy's Obtained from Different Polymerization Systems

Polymerization System	Elemental Compositions (Atomic Ratio)	Yield (%)	Conductivity (S cm^{-1})
Solution	$\text{C}_{4.012}\text{H}_{3.101}\text{N}_1\text{Fe}_{0.061}\text{Cl}_{0.233}\text{S}_{0.011}$	62.7	0.13
Emulsion	$\text{C}_{3.986}\text{H}_{3.064}\text{N}_1\text{Fe}_{0.063}\text{Cl}_{0.225}\text{S}_{0.011}$	75.8	0.96
Microemulsion	$\text{C}_{4.034}\text{H}_{3.087}\text{N}_1\text{Fe}_{0.062}\text{Cl}_{0.237}\text{S}_{0.013}$	92.2	2.09

Electrical conductivities of powders were measured on dried pressed pellets employing the conventional four-probe method under laboratory conditions.

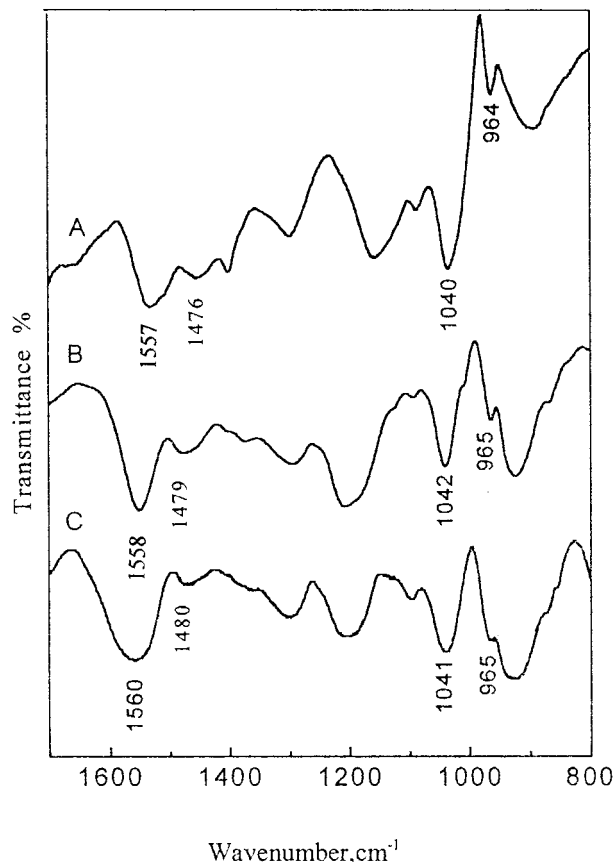


Figure 2 FTIR spectra of PPy particles obtained from the chemical polymerization systems: (A) solution; (B) emulsion; (C) microemulsion.

integrated peak intensities of 1560 cm^{-1} against 1480 cm^{-1} are associated with the $\text{C}=\text{C}/\text{C}-\text{C}$ stretching mode of PPy, which relates to the effective mean π -conjugation along the polymer chains, namely, the stronger the peak intensity at 1560 cm^{-1} , the longer the conjugation length of the PPy backbone.^{28,29} On closer inspection of the spectra of the polymers, it can be found in Figure 2(C) that the integrated peak intensity of 1560 cm^{-1} against 1480 cm^{-1} ($I_{\text{C}=\text{C}/\text{C}-\text{C}}$) is the maximum, indicating that the PPy synthesized in the microemulsion has the longest effective conjugation length. The results of the FTIR spectra are in good agreement with the result of the conductivity measurement.

Some more supporting evidence of the structures of the PPy's was found by the TGA-DTA experiments, as shown in Figure 3. Figure 3(A) shows the thermal stability of PPy synthesized in solution. It can be seen that the first small fractions of weight loss from room temperature to

about 120°C is due mainly to the expulsion of absorbed water from the polymer samples (since it is difficult to remove the moisture in the samples completely). Up to 269°C , there is little weight loss, indicating good thermal stability, and then a very significant weight loss begins to occur at 269°C due to the thermal oxidative decomposition of molecular main chains. In Figure 3(B), a relatively higher decomposition temperature of PPy synthesized in the emulsion is observed at about 273°C , indicating better thermal stability. Figure 3(C) shows a thermogram of PPy synthesized in the microemulsion. It can be clearly seen that a very significant thermal degradation occurs at about 278°C , implying that the sample has the best thermal stability among the three samples. According to the reported literature,³⁰ the highest decomposition temperature may again be due to longer conjugation chain segments in the PPy polymer units, and this result confirmed the result of the FTIR spectra studies. The TGA-DTA patterns clearly indicate a good thermal stability of the PPy synthesized in the microemulsion system, and it is of special significance to several applications of conducting PPy where high thermal stability is essential.³¹

It should be noted that in Figure 3(C) a sharp exothermic peak at about 305°C occurred. According to the literature, this sharp exothermic peak may be associated with some morphological change of the polymer,³⁰ implying a much more ordered arrangement of the macromolecule chains of PPy synthesized from microemulsion polymerization. Based on the reported works,^{20,21} it can be assumed here that in the microemulsion system the pyrrole monomer present in the microdroplets and the molecular chains of the monomer and oligomer are molecularly oriented by the surfactants in the interface layer of the oil and water phases. Following this alignment, the radicals of the PPy oligomers coupled to form a conducting polymer, which results in PPy with a longer effective conjugation length and the ordered arrangement of the macromolecule chains. Since the concentration of surfactants in conventional emulsion polymerization is relatively lower in comparison with the microemulsion polymerization system, the orienting effect of the surfactant in the emulsion polymerization is not significant and even can be neglected in this work. In the homogeneous solution system, molecular chains of the pyrrole monomer are randomly aligned, which resulted in the amorphous polymer.

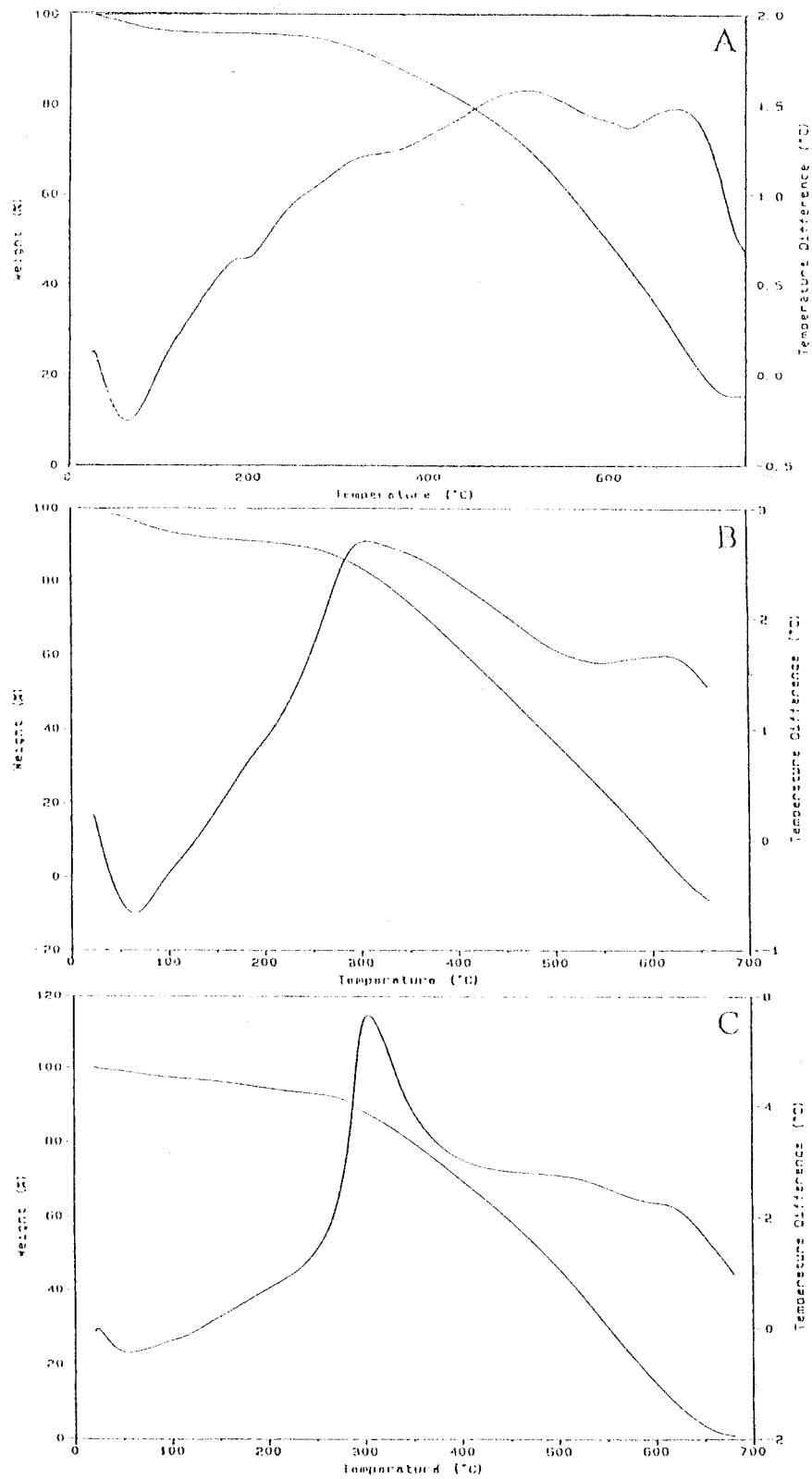


Figure 3 TGA-DTA thermograms of PPy's in air synthesized from (A) solution, (B) emulsion, and (C) microemulsion.

CONCLUSIONS

In conclusion, pure nanoscopic conducting PPy was successfully synthesized in the oil/water microemulsion. During the microemulsion polymerization, the reaction system is quite stable, without any evident precipitation. Compared with the homogeneous solution and conventional emulsion polymerizations, the microemulsion polymerization system increases the yield of the resultant PPy. Characterizations of the polymers mentioned above show that the molecularly ordered microemulsion system increased the extent of the π -conjugation along the polymer backbone and ordered the arrangement of the macromolecule chains; these two effects bring about enhanced conductivity as well as higher thermal stability of PPy. Improvement of the electric conductivity of PPy and further investigations on the preparation of PPy in ternary microemulsion systems (without cosurfactants) are in progress in our laboratory.

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