

Non-aqueous core-shell dispersion with a cross-linked acrylic core and poly(aniline)/DBSA shell

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Summary

The electrically conductive microgel coated with PANI-DBSA was prepared in organic media containing polymeric microgel and dodecylbenzenesulfonic acid (DBSA) using ammonium persulfate (APS) as an oxidant. According to the images of the transmission electron microscopes, the prepared conductive microgel has a core-shell microsphere, which is composed of cross-linked acrylic core and PANI-DBSA shell. The particle size of the prepared conductive microgel ranges in 80~90 nm. The electrical conductivity can reach values as high as 0.2~0.8 S/cm. The highly conductive transparent film could be notably obtained by using small amount of non-aqueous conductive microgel.

Introduction

A number of applications of electrically conductive polymers for surface tension control, electromagnetic wave shielding, fuel batteries, etc. have been under study [1-3]. Particularly, poly(aniline) (PANI), poly(pyrrole), and poly(thiophene) are stable in air with high electrical conductivity. Another advantage of these conductive polymers is that they can be easily synthesized through electrochemical or chemical polymerization [4-5]. However, films made of the electrically conductive polymers synthesized through electrochemical polymerization, although being constant in electrical conductivity across their surface areas, are greatly limited in uses because they are not easily melted owing to the strong intermolecular attractive force thereof. Powders of the electrically conductive polymers synthesized through chemical polymerization also require complicated post-treatment procedure for their applications.

Recently, extensive researches have been directed to improving the processability of electrically conductive polymers such as substituted derivatives, colloidal dispersions and composite particles. One of these attempts to improve processability is the preparation of PANI in colloidal. In 1989, Ames et al. reported that the colloidal

PANI had been prepared by using polymeric surfactant. These systems significantly enhance the processability of the normally intractable PANI [6]. Cao et al. reported that PANI doped with dodecylbenzenesulfonic acid (DBSA) or camphor sulfonic acid could be soluble in various organic solvents such as chloroform and xylene [7]. Wiersma et al. have shown that sterically stabilized latex particles can be coated with poly(pyrrole) or PANI in aqueous media to form conducting polymer coated latexes with good colloid stability [8-9]. Recently, Kuramoto and Tomita reported chemical oxidative polymerization of DBSA aniline salt resulted in aqueous suspension and homogeneous chloroform suspension [10-11]. On the other hand, some groups have reported the tailor-made composite particles blended with vinyl polymers. In 1987, Yassar et al. reported aqueous suspension of poly(styrene) latex particles coated with poly(pyrrole)[12]. Barthet et al. reported that poly(N-vinylpyrrolidone)-stabilized poly(styrene) latexes had been coated with thin overlayers of PANI to produce electrically conductive core-shell particles[13]. More recently, Okubo et al. synthesized a micron-sized, mono-dispersed, core-shell poly(styrene)/PANI composite particles by chemical oxidative seeded dispersion polymerization[14].

In this report, the electrical conductive microgel coated with PANI-DBSA was prepared in organic media containing polymeric microgel and DBSA using ammonium persulfate(APS) as an oxidant. The preparation method of the electrical conductive microgel does not require tedious cleanup operations such as centrifugation and redispersion. The prepared conductive microgel has a structure of the core-shell microsphere, which is composed of cross-linked acrylic core and PANI-DBSA shells, to give non-aqueous dispersion in organic solvent. We also could prepare transparent conductive films using small amount of the prepared conductive microgel.

Experimental

Preparation of Non-aqueous Microgels Dispersion[15-16]

360 g deionized water and 3.2 g rhodapex co-436 (Rhodia Co.), emulsifier, are placed in thermo regulated jacketed vessel at 80 °C. A monomer mixture of 30 g n-butyl acrylate, 50g of methyl methacrylate and 2g of allyl methacrylate is added within 2 hours with stirring. Simultaneously, an initiator solution consisting of 1.1 g APS and 20 g deionized water are added drop wise within 3 hours. After the reaction, an aqueous microgel dispersion having solids content of 17.6% and particle size of 67 nm is recovered.

466.3g of the above microgel dispersion is allowed to react with 222g of n-butanol with stirring. After 12 hours, 2 phases are formed of which the lower phase, consisting of 344g of n-butanol saturated water, is discharged. The upper phase containing the microgel is a non-aqueous microgel dispersion having a solids content of 24.6 % and an average particle size of 88.6 nm. The swelling ratio, q , of the non-aqueous microgel was calculated to give 2.31 as $(D_b/D_w)^3$, where D_b and D_w are the hydrodynamic particle size in n-butanol and in water, respectively[17]. The particle size of the microgel was measured by a Coulter N4M sub-micron particle analyzer.

Preparation of conductive microgel coated with PANI

19.6 g (0.21 mol) of aniline was polymerized in the mixture of 345g of butyl acetate,

411.8 g of the above microgel solution and 68.6 g (0.21 mol) of DBSA with 57.5 g (0.25 mol) of APS solution in 600g of water as an oxidant. During the addition of APS solution drops was added, the temperature was kept below 10 °C. After addition of APS solution, the color of the microgel changed to blue and then to dark green. Polymerization of aniline was also carried out chemically in solution with different weight ratios of aniline-DBSA/microgel. After reaction, 2 phases are formed of which the lower phase containing the oxidized APS is discharged. The upper phase containing the conductive microgel coated with PANI has solid content of 15%.

Characterization of conductive microgel

Conductivity was measured at 20 °C using conventional four-point probe techniques. Transmission electron microscopy studies were made on dilute dispersions dried down on carbon-coated copper grids(from Bio-Rad) using a JEOL-100 C instrument. The morphology of the conductive microgel films was studied with field emission scanning electron microscopy (FE-SEM, JEOL model JSM-6340F). The transmittance of the dried conductive microgel films was measured by the UV-vis spectrometer (Verian-3-Bio) as prepared.

Results and discussion

The non-aqueous conducting microgel is prepared in following manner. Aniline, monomer of the electrically conductive polymer, is added to non-aqueous acrylic microgel solution. In the presence of polymerization catalyst, aniline is polymerized to form an electrically conducting polymer. In this process, aniline can polymerize at the interface of water and non-aqueous microgel solution to form an electrically conductive oligomer or polymer, which is poorly soluble in the dispersing medium. Therefore the formed oligomer or polymer is precipitated onto the cross-linked microgel. As a result, a non-aqueous conducting microgel is obtained, which contains an electrically conductive polymer that is substantially adsorbed on the surface of the cross-linked acrylic microgel. The prepared conductive microgel is presumably formed as a thin layer at the surface of the non-aqueous microgel without significant interfering by the steric stabilization(Figure 1). In addition, the dispersion of electrically conductive particles may contain freely present electrically conductive polymer in the dispersing medium.

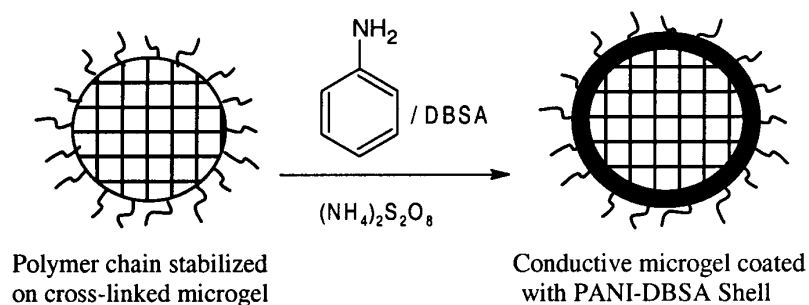


Figure 1. Schematic representation of the deposition of PANI-DBSA on cross-linked microgel.

Figure 2 shows the effect of varying the ratio of aniline-DBSA to non-aqueous conductive microgel on the conductivity. The electrical conductivity of the range of

0.2-0.8 S/cm was obtained, when the ratio of aniline-DBSA/non-aqueous conductive microgel was above 0.35, with no indication of sharp percolation threshold. The conductivity increased with increasing the ratio of PANI-DBSA/non-aqueous conductive microgel and became level off at the ratio larger than 0.30. The observed conductivities were invariably less at least an order of magnitude than that of the corresponding bulk powder of the PANI-DBSA. This is due to the presence of resistive interparticle contacts at the nano-scale level. Conductivity of PANI also depends on the molar ratio of oxidant to aniline-DBSA. The conductivity increases as the molar ratio of the oxidant to aniline increases. This results is consistent with that of Kuramoto's works [10]. When the molar ratio exceeds 1.2, the polymerization yield decreases, presumably due to over-oxidation of PANI chains with concomitant formation of low-molecular weight by-products.

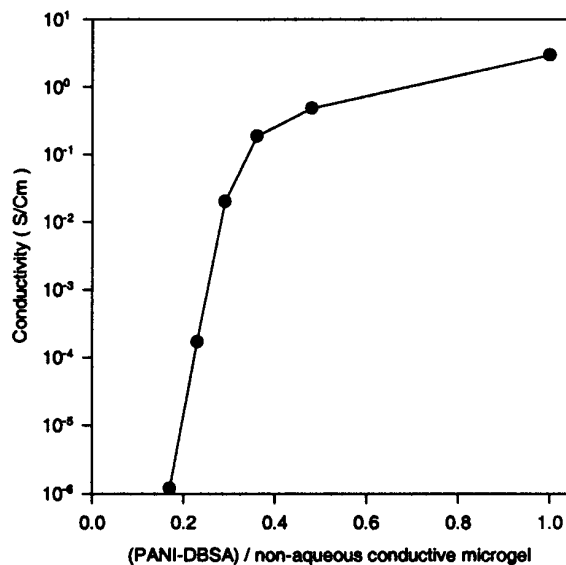


Figure 2. Effect of the ratio of PANI-DBSA/non-aqueous conductive microgel on the conductivity.

The morphology of the non-aqueous polymer microgel coated with PANI-DBSA in this study is core-shell spherical and fairly monodisperse as evidenced by transmission electron microscopy. A typical transmission electron micrograph of a dried, diluted and non-aqueous conductive microgel is shown in Figure 3. This micrograph clearly shows the structure of the core-shell microsphere with 80-90nm of particle size. The dark and white portions of microsphere indicate the cross-linked acrylic cores and PANI-DBSA shells, respectively. Varying the size of the cross-linked acrylic cores can easily control particle size. Similar spherical morphologies have been reported for polymer-stabilized poly(pyrrole) colloids by Wierma et al [8]. However, as far as we know, this is the first report regarding the formation of the core-shell structure for non-aqueous colloidal PANI.

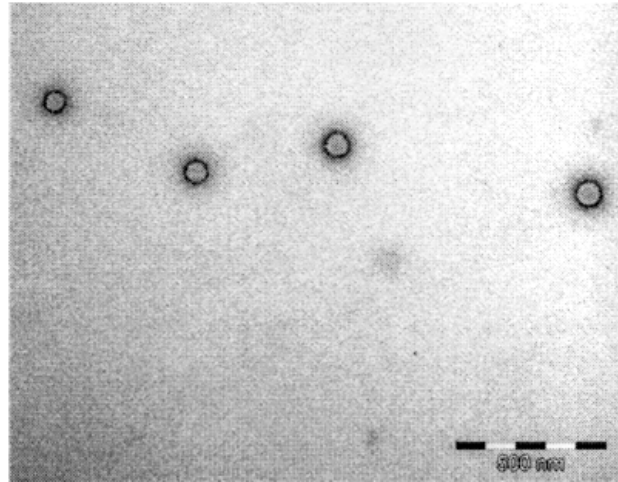


Figure 3. Transmission electron micrograph of non-aqueous microgels coated with PANI/DBSA. (magnification 50000 \times)

Because the prepared conductive microgel is well dispersed in organic media such as n-butanol and butyl acetate with nano-scale particle, the conductive microgel solution itself can be easily processed in the optical transparent films. As shown in Figure 4, highly transparent films in the $10^3 \sim 10^5$ ohms/square range could be prepared with various film thickness. During film formation the PANI-DBSA shell can easily form a conductive pathway, resulting in a conductive film.

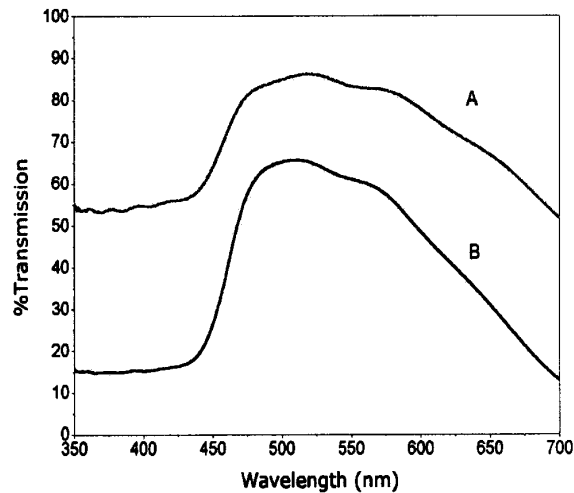


Figure 4. Transmission curves for the conductive microgel applied film with varying film thickness (A: surface resistance $3.5 \times 10^4 \Omega/\text{sq}$ with film thickness $1.1 \mu\text{m}$, B: surface resistance $6.7 \times 10^3 \Omega/\text{sq}$ with film thickness $3.3 \mu\text{m}$)

Examination of the dried-down conductive microgel solution by scanning electron microscopy reveals a morphology, which consists of rice grain particles as shown in Figure 5. Because the glass transition temperature of the cross-linked acrylic core is as

low as 24 °C, the spherical shape of the conductive microgel is, presumably, deformed and reformed to a rice grain particle as solvent evaporates during film formation. In addition, the cross-linking density of acrylic core can also effect on the deformation to the rice grain morphology. The cross-linking density, defined as the molar concentration of the difunctional monomer[allyl methacrylate] in the total monomer solution, is found to be inversely proportional to the swelling ratio. In our study, the cross-linking density and the swelling ratio of acrylic core were 3.4×10^{-4} (mol/g) and 2.31 respectively [18-19]. It is assumed that the morphology change from sphere to the rice grain shape can give more efficient conductive pathway than spherical particle in the applied film.

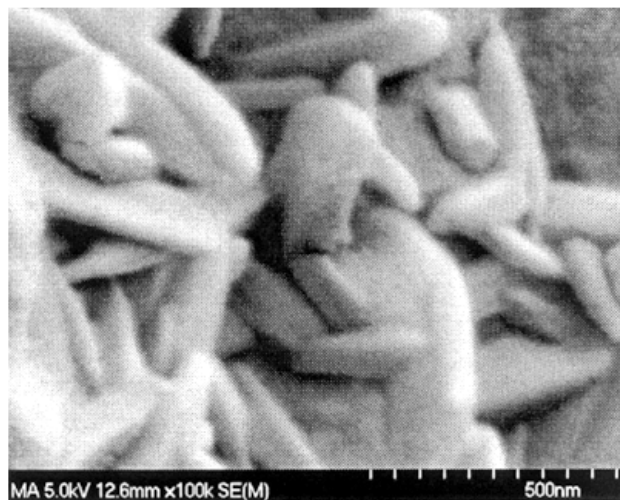


Figure 5. Scanning electron micrograph of the dried films of non-aqueous microgel coated with PANI-DBSA

Conclusions

The electrically conductive microgel coated with PANI-DBSA was prepared in organic media containing polymeric microgel and DBSA using APS as an oxidant. According to the images of the transmission electron microscopes, the prepared conductive microgel has a core-shell microspheres, which is composed of cross-linked acrylic core and PANI-DBSA shell. The particle size of the prepared conductive microgel ranges in 80~90 nm. The electrical conductivity can reach values as high as 0.2~0.8S/cm. The highly conductive transparent film could be notably obtained by using small amount of non-aqueous conductive microgel. In addition, we have obtained similar results to the other conductive monomers such as pyrrole and 3,4-ethylene dioxythiophene, and are now searching for the optimum conditions to increase conductivities and colloidal stability. Those results will be reported elsewhere [20].

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