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Short communication

Tuning the morphologies of conducting polyanilines using sulfonic acid-containing Gemini surfactants with different spacer lengths

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ABSTRACT

A novel method was used to tune the morphologies and properties of conducting polyanilines. In the first time, sulfonic acid-containing Gemini surfactant 9BA-*m*-9BA (that is 6,6′-(alkyl-1,*m*-diylbis(oxy))bis(3-nonylbenzenesulfonic acid) with different alkyl spacer length $m = 2, 3, 4, 6$, respectively) was used in the preparation of conducting polyanilines at 0 °C in reverse emulsion system of ethyl acetate/water with the volume ratio of 10:1. Simply increasing the spacer length of 9BA-*m*-9BA from $m = 2$ and 3 to $m = 4$ and 6, the morphologies of resultant polyanilines were changed obviously from granular to fiber-like forms, while the intrinsic viscosity of resultant polyanilines increased dramatically from 49.3 to 119.5 ml/g but conductivity decreased from 1.0 to 0.1 S/cm.

1. Introduction

Polyaniline is considered as one of the most attractive conducting polymers because of its good environmental stability, desirable electrical, electrochemical properties, and ease of synthesis [1]. Recently, nanostructured conducting polyanilines have been extensively studied because of their unique properties and promising applications as nanomaterials and in nanodevices [2]. Shape and size of these nanomaterials were found very crucial for their functioning in electronic devices and biosensor applications [3]. Various nanostructured polyanilines (nanofibers/tubes/wires/rods) have been prepared by electrospinning, hard templates, soft templates, interfacial polymerization, dilute polymerization, seed polymerization, etc. [4]. In particular, soft-template method is an relatively simple, cheap and powerful approach, and many kinds of surfactants including dodecylbenzene sulfonic acid (DBSA), dinonylnaphthalenesulfonic acid (DNNSA), sodium dodecylbenzene sulfonate (SDBS) and sodium dodecylsulfate (SDS) have been used as soft-template to prepare nanostructured polyanilines with different morphologies because the structure of the surfactant is crucial for the stabilization of formed micelles and the morphology of resultant polyanilines [5]. Though the various approaches have been established, the preparation of conducting polyaniline with deliberate control of morphologies and sizes is still a major challenge.

In this communication, a series of sulfonic acid-containing Gemini surfactants, 6,6′-(alkyl-1,*m*-diylbis(oxy))bis(3-nonylbenzenesulfonic acid) (9BA-*m*-9BA, Fig. 1A) with different alkyl spacer length $m = 2, 3, 4, 6$, that is, 6,6′-(ethane-1,2-diylbis(oxy))bis(3-nonylbenzenesulfonic acid) (9BA-2-9BA), 6,6′-(propane-1,3-diylbis(oxy))bis(3-nonylbenzenesulfonic acid (9BA-3-9BA), 6,6′-(butane-1,4-diylbis(oxy))bis(3-nonylbenzenesulfonic acid) (9BA-4-9BA), and 6,6′-(hexane-1,6-diylbis(oxy))bis(3-nonylbenzenesulfonic acid (9BA-6-9BA), were synthesized and used in the preparation of conducting polyanilines. The change of alkyl spacer length of Gemini surfactant plays a great influence on the morphology and properties of resultant polyanilines.

So-called Gemini surfactant contains two hydrocarbon chains and two hydrophilic head groups covalently connected by spacer chain at the level of, or near to the hydrophilic head groups, which generally shows significantly lower critical micelle concentration (CMC) and greatly increased surface activity when compared to the conventional monomeric surfactants of similar chain length and head group [6,7]. It is found that Gemini surfactants are of particularly interests in the polymerization of styrene in ternary microemulsion because the surfactant shape, aggregation properties, and thus the interfacial spontaneous curvature can be easily "tuned" by changing the spacer length of the Gemini surfactants and lead to nanolatex particles with controlled properties [6]. The spacer length in the Gemini surfactants decisively influences the microemulsion formation. However, sulfonic acid-containing Gemini surfactant used in the aniline polymerization as the stabilizer and dopant of resultant polyanilines simultaneously is not yet investigated till now.

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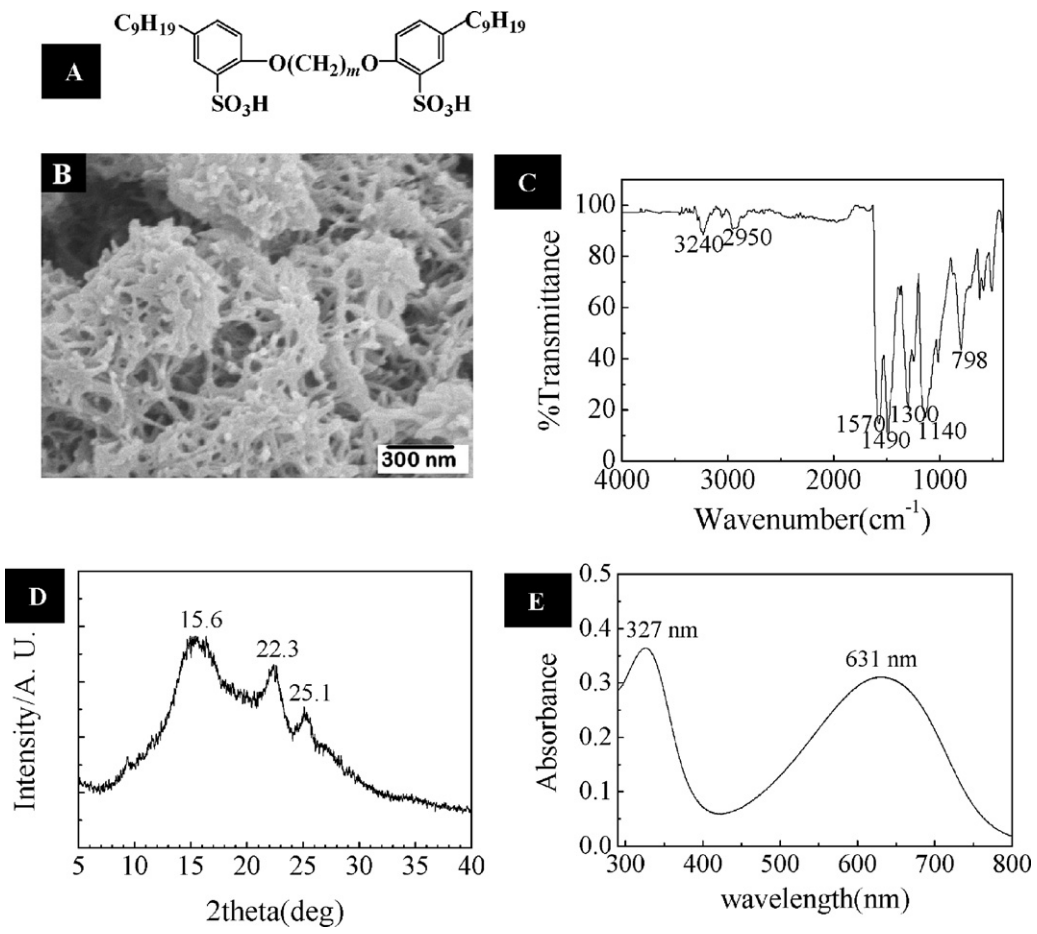

Fig. 1. Polyaniline synthesis using Gemini surfactants: (A) the structure of used Gemini surfactant 9BA-*m*-9BA (6,6′-(alkyl-1,*m*-diylbis(oxy))bis(3-nonylbenzene-sulfonic acid, *m* = 2, 3, 4, 6, respectively); (B–D) SEM image, FTIR and XRD results of resultant polyanilines prepared in the polymerization system with 9BA-4-9BA as surfactant, respectively; (E) UV–vis spectrum of resultant polyanilines in emeraldine base in NMP prepared in the polymerization system with 9BA-4-9BA as surfactant.

2. Experimental

2.1. Materials

Aniline (Shanghai Wulian chemical engineering factory, China) was distilled under reduced pressure, and stored at low temperature prior to polymerization. Ammonium persulfate (APS) was purchased from Beijing chemical engineering factory, China. Nonylphenol and chlorosulfonic acid (Beijing Chemical Industry Corporation, China) were stored at low temperature prior to use. 1,2-Dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane (Shanghai Chemical Reagent Company, China), 1,6-dibromohexane (Alfa Aesar, USA) and other chemicals were used as received without further purification. Distilled water was used in all experiments.

2.2. Preparation of polyanilines in EB form

The synthesis and characterization of 9BA-*m*-9BA are described elsewhere [8]. Polyaniline was typically synthesized using peroxydisulfate (APS) oxidant in the reverse emulsion system of ethyl acetate/water with the volume ratio of 10:1 at 0 °C. The reverse emulsion system was prepared by adding 4.0 mmol of 9BA-4-9BA to 80 ml of ethyl acetate, and followed by the dropwise addition of 8.0 mmol aniline in 6 ml of water. The mixture was kept mechanical stirring for 1 h in an ice bath. The polymerization was initiated by dropwise adding 8.0 mmol APS in 2.0 ml of water to above emulsion system. The molar ratio of 9BA-4-9BA/aniline/APS was 0.5/1.0/1.0. After being stirred at 0 °C for 24 h, ethanol was added to give the dark green polyaniline precipitate. The precipitates were filtered, washed, and dried under dynamic vacuum. Part of above dark green polyaniline precipitate was treated in 10% aqueous ammonia for 4 h at the room temperature to give the polyaniline in emeraldine base form.

2.3. Property characterizations

The intrinsic viscosities of the polyanilines in emeraldine base form were determined at 0.4% (wt./vol.) polymer in 98% concentrated H_2SO_4 using Ubbelohde viscometer at 30.0 ± 0.1 °C. Experiment was carried out at four gradually diluted concentration, and the intrinsic viscosity could be obtained by extrapolating the line of specific viscosity divided by the c (η_{sp}/c) vs c and the line of the natural logarithm of relative viscosity divided by c ($\ln \eta_{rel}/c$) vs c to the same intercept at zero concentration.

Electrical conductivities of the resultant polyaniline salts were measured on dried pressed pellets at room temperature using the four-point probe technique. FTIR spectra of the polyanilines were recorded by a Nicolet NEXUS-470 FTIR spectrophotometer with the KBr pellet technique. UV–vis absorptive spectra of the polyanilines in N,N′-methyl-2-pyrrolidone (NMP) were obtained from GBC UV–Vis cintra 10 spectrometer in 300–900 nm. Wide-angle X-ray diffraction (WAXD) patterns of polyanilines were taken with Ni-filtered Cu Kα radiation using Rigaku DMAX2200 with the scanning range from 5 to 60° and the X-ray power of 40 kV and 40 mA.

Morphology studies of polyaniline samples were carried out using FE-SEM JSM 6700 scanning electron microscope (SEM) oper-