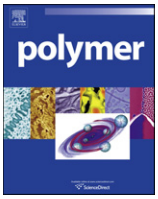
Polymer 49 (2008) 4218–4225

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Formation mechanism of a nanotubular polyanilines prepared by an emulsion polymerization without organic solvent

Bi-Zen Hsieh [a], Hung-Yi Chuang [a], Liang Chao [b], Yu-Jen Li [a], Ying-Jie Huang [c], Po-Hao Tseng [d], Tar-Hwa Hsieh [a], Ko-Shan Ho [a,*]

[a] *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kuo Road, Kaohsiung 807, Taiwan, ROC*
[b] *Center for General Education, Technology and Science Institute of Northern Taiwan, Peito, Taipei 11202, Taiwan, ROC*
[c] *Institute of Nanotechnology, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu, Taiwan, ROC*
[d] *Ming-Dao High School, 497, Section 1, Chung-San Road, Wu-Zi County, Taichung, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 27 March 2008
Received in revised form 30 June 2008
Accepted 3 July 2008
Available online 15 July 2008

Keywords:
Polyaniline
Nanotube
Emulsion polymerization

ABSTRACT

A nanotubular polyaniline (PANINT) was prepared from a simple emulsified polymerization method without oil solvent present. A mechanism of the formation of the nano-fibers/tubes was proposed to show that it started with the connecting arrangement of the neighboring anilinium micelles before and during polymerization, which resulted in the formation of the intermediate morphology of centipedes converting into rod-like nanofibers later. The obtained PANINTs displayed not only nanofibrous structure but owned an unusual dispersing behavior in toluene. SEM and TEM showed the dendrite-like networks of nanofibers connected and glued together by the free (not complexed to polyaniline backbone) *n*-dodecylbenzene sulfonic acid (DBSA) molecules. After removing the free DBSA by acetone, the clear/well-defined empty nanotubes can be seen from TEM in the magnified micrograph. The Atomic force microscopic (AFM) micrographs demonstrated the cottage like surface morphology of the un-perturbed PANINTs and the morphology was converted to an anisotropic/oriented rods after rubbing on the wet/cast PANINTs' dispersion of toluene before entire evaporation.

© 2008 Published by Elsevier Ltd.

1. Introduction

Polyaniline (PANI) is a typical conducting polymer that has been found lots of applications in the field of biosensors [1], electrochemical displays [2], corrosion protection [3,5], rechargeable batteries [4,6], etc. Traditional way of synthesizing PANI via chemical oxidize [7–10] or electrochemical route [9] came out with particle-accumulated cluster morphology. In order to obtain a PANI with higher reactive surface area, higher ordered structure, and higher conductivity, a nanofibrous or nanotube-like structure is necessary. Traditional chemical oxidative polymerization approaches for nano-structured polymers include the use of insoluble solid templates such as zeolites [11], opals [12], controlled pore-size membranes [13], and anodic aluminum oxide (AAO) [14] or soluble templates such as polymers [15] and surfactants [16]. Some physical methods, such as electrospinning [17] and mechanical stretching [18] can also produce conducting polymer nanofibers without templates. When organic dopants with surfactant functionalities are used, emulsions or micelles can be formed leading to microtubes, -fibers, or -rodlike structures [19–23]. Kaner and coworkers prepared nanofibrous PANI by interfacial polymerization with aniline monomers soluble in an organic solvent [23,24]. Haba et al. reported a nanofibrous morphology of DBSA doped polyaniline originated from the filling of the nanopores of the polyaniline spherical particles into nanorods without the presence of any organic solvent with low conductivity due to the absence of the strong acid to gain high degree of doping [25]. Additionally, other novel methods like sonochemical [26] and gamma irradiation [27] methods were also used for the preparation of the nano-structure of polyanilines.

The presence of the large amount of long alkyl protonic acid dopant to maintain the lower pH value for polymerization did give us a nanofibrous conformation of polyaniline via emulsion polymerization. However, the nanofibers can only be seen after washing with lots of organic solvents and the conductivity is so good due to the lower degree of doping of mild acid nature of DBSA. Stejskal et al. proposed the presence of the phenazines in the early stage of polymerization when the pH value is not too small. The phenazines behaved as the tubular nuclei for the formation of helical polyanilines into nanofibers in the later stage with lower pH values [28–30]. We are going to present an easy method of emulsion-polymerizing (the aqueous initiators are actually starting the

---

[*] Corresponding author. Tel.: +886 7 381 4526; fax: +886 7 383 0674.
E-mail address: hks@cc.kuas.edu.tw (K.-S. Ho).

0032-3861/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2008.07.008

polymerization at the hydrophilic outer part of the micelles) anilinium monomer micelles into polyaniline nanotubes (PANINTs) without using any organic solvent in the presence of two different dopants, HCl and DBSA to obtain a nanofibrous polyaniline with high conductivity. In our studies, the pH values were already low in the beginning of polymerization due to the presence of large amount of hydrochloric acid in the reaction mixtures. Therefore, the nucleation of a nanotubular polyaniline was not resulted from the formation a phenazine as nucleus. A supramolecular structure of the formed anilinium micelles will be proposed, which can explain the formation of the centipede-like and helical nanofiber/tubes of the resultant polymers. All kinds of electronic microscopies such as SEM, TEM, and AFM were used to characterize various nano-polyaniline molecules.

2. Experimental part

2.1. Preparation of PANINTs

To dissolve 3 g (0.091 mol) *n*-dodecylbenzenesulfonic acid (DBSA: Tokyo Kasei Kogyo Co.) in 50 ml de-ionized water, the mixture was slowly stirred until a homogeneous solution was formed, then 9 g (0.0968 mol) aniline monomer (Tokyo Kasei Kogyo Co.) was added and kept stirring to become emulsified then 9 ml, 1 M HCl (Riedel-de Haën) was mixed with mixture, linking the micelles together and enhancing the emulsification. The mixture became less transparent with the addition of HCl. An ammonium persulfate (APS: Showa Chemicals Instrument Co.) aqueous solution prepared in another beaker by dissolving 7.33 g (0.0323 mol) APS in 30 ml de-ionized water was kept in low temperature in a freezer several hours before using and was poured directly into the reaction mixture followed by a vigorous stirring with a magnetic stirrer. With the proceeding of the polymerization, the temperature rose up quickly after 10–15 min, followed by the darkening of the reaction mixture and the polymerization was proceeded for 3 hrs before polyaniline was isolated by filtration, followed by washing with some isopropanol and the obtained filter cakes were dried in an oven at 60 °C for 12 h.

2.2. Preparation of PANINT dispersion of toluene

A 0.5 g PANINT powder was mixed with 10 ml toluene and zirconium oxide mini-balls in a cell for vibrating ball-milling. The cell was vibrated in a ball-miller (Retsch MM301) three times with 10 min for each interval to become a well-dispersed state of dispersion.

2.3. Polarized optical microscopy (POM)

Emulsified monomers solution was cast on a microscope glass plate (7.6 × 2.54 × 0.1 cm) and covered with cover glass to prevent the evaporation of water and taken polarized optical micrograph by Olympus BH-2 optical microscope.

2.4. Scanning electron microscopy (SEM)

Samples of PANINTs and EB type were taken micrograph in a Field emission SEM, HR-SEM (Hitachi S-4200: accelerating voltage of 15 kV) prepared from strewn on carbonic tape and followed by posting on ferric stage.

2.5. Transmission electron microscopy (TEM)

Samples for Field emission transmission electron microscopy, HR-AEM (Hitachi FE-2000) were prepared from acetone dispersion and dropped on carbonic-coated copper grids.

2.6. Atomic force microscopy (AFM)

Samples for Atomic force microscopy, AFM (CSPM 4000) were PANINTs dispersion cast directly onto a glass plate.

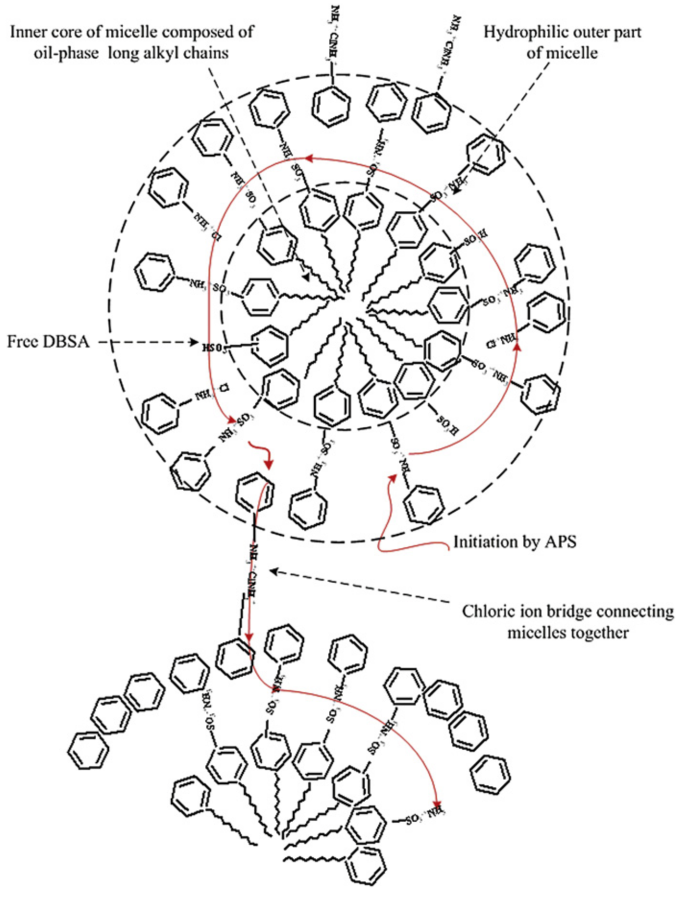
2.7. Conductivity

A 4-probes Milliohm meter (LUTRO MO-2001) was used to measure the conductivity of PANINT powders which were pressed into tablets.

3. Results and discussion

3.1. Mechanism

The anilinium monomer micelles were derived from the complexation of aniline with first DBSA then HCl in the aqueous mixture and no anilinium ions were present in the inner cores of micelles composed of hydrophobic long alkyl tails as depicted in Scheme 1. The anilinium ions countered with the aqueous ends of DBSA stayed and well distributed in the outer part of micelles. When HCl was introduced, the micelles were further expanded by the insertion of the HCl complexed anilinium ions that pointed outward due to their hydrophilic nature of the chloric counter ions. Before HCl was introduced, the DBSA-complexed anilinium emulsion solution was cloudy white (Fig. 1(a)) with a smaller, averaged micelle size of around 246 nm (Fig. 2). The introduction of the hydrochloric acid enlarged the size 1000 times to 392.8 μm from 246 nm (Fig. 2(b)) with neighboring micelles connected together and the emulsification was then enhanced through chloric ions' bridges as described in Scheme 1. Then sudden increase of size attributed from the



Scheme 1. Schematic diagram of micelles.

Download English Version:

https://daneshyari.com/en/article/5185291

Download Persian Version:

https://daneshyari.com/article/5185291

Daneshyari.com