J. of Supercritical Fluids 47 (2008) 103–107

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Preparation of polyacrylonitrile nanofibers as a precursor of carbon nanofibers by supercritical fluid process

Jun Ho Kim[a], Hullathy Subban Ganapathy[a], Seung-Soo Hong[b], Yeong-Soon Gal[c], Kwon Taek Lim[a,*]

[a] Division of Image and Information Engineering, Pukyong National University, San100 Yongdang-dong, Nam-gu, Busan 608-739, Republic of Korea
[b] Division of Applied Chemical Engineering, Pukyong National University, Busan 608-739, Republic of Korea
[c] Polymer Chemistry Laboratory, College of Engineering, Kyung Il University, Gyeongsang buk-do 712-701, Republic of Korea

ARTICLE INFO

Article history:
Received 5 February 2008
Received in revised form 9 May 2008
Accepted 29 May 2008

Keywords:
Carbon materials
Nanofibers
Polyacrylonitrile
RESS
RESOLV
Supercritical fluids

ABSTRACT

A simple method for the preparation of polyacrylonitrile (PAN) nanofibers using a supercritical fluid technique, rapid expansion of a supercritical solution into a liquid solvent, is reported. It was found that PAN fibers having the size range of 50–300 nm in diameter were obtained when a solution of supercritical carbon dioxide and dimethylformamide mixture containing PAN was rapidly expanded into an ambient aqueous NaCl solution, at a pre-expansion pressure and temperature of 20.7 MPa and 60 °C, respectively. The effect of polymer concentration on the formation of nanofibers vs. nanoparticles was investigated. The morphological analysis by field emission scanning electron microscopy revealed that PAN nanofibers were exclusively obtained at higher polymer concentrations whereas aggregated nanoparticles were produced by lower concentrations of PAN in the supercritical solution. Using the PAN nanofibers as precursors, carbon nanofibers were obtained by the pyrolysis at 800 °C under N_2 atmosphere.

1. Introduction

Carbon nanofibers (CNFs) have been receiving increasing attention because of their high length-to-diameter ratio and their potential applications in composite materials, templates for nanotubes, filters, gas storage systems (mainly hydrogen), anode materials for rechargeable batteries, supercapacitors, bottom-up assembly in nanoelectronics, etc. [1–4]. The oxygen-containing activated sites of CNFs and the physiochemical properties such as conductivity, large surface area, and biocompatibility could be ideal for immobilization of biomaterials suggesting their promising biomedical applications in cellular impalement and gene delivery [5]. Among the materials used in the preparation of CNFs, polyacrylonitrile (PAN) and its copolymers are recognized as the most promising precursors [6]. In general, a number of methods are available for the preparation of polymeric nanofibers, though the most widely used one is electrospinning [7]. Others, such as template-guided polymerizations including the use of zeolite channels, nanoporous membranes, and block copolymer micelles have been used for the preparation of nanofibers [8–10]. The advantages and limitations of these methods have been evaluated recently [7,11]. Widely discussed disadvantages of above methods are multi-stage processing, excessive use of templates that sometimes resulted in unwanted residues in the final product, etc.

Herein, we report a simple method to prepare PAN nanofibers by using environmentally benign solvent, supercritical carbon dioxide ($scCO_2$). Because CO_2 is nontoxic, nonflammable, and environmentally friendly, $scCO_2$ technology has recently played a significant role in particle engineering [12]. In general, the rapid expansion of supercritical solutions (RESS) containing solutes through a small heated micro-orifice, produce an abrupt decrease in dissolving capacity of the $scCO_2$. The high degree of supersaturation accompanying the rapid depressurization into a region of much lower pressure results in homogeneous nucleation and thereby ultra-fine particles are produced. It is well known that RESS generally produces micrometer-sized particles as primary products, because of the particle growth process of efficient condensation and coagulation inside the expansion jet [13]. Under well-controlled conditions, RESS is also known to produce polymeric microfibers [14–16]. However, Meziani et al. have recently reported the formation of exclusive polymeric nanoparticles and nanofibers by a modified RESS method, known as the rapid expansion of a supercritical solution into a liquid solvent (or RESOLV) [17,18]. Very recently, we have also reported the preparation of semiconducting polymeric nanoparticles by RESS and RESOLV methods [19–21]. Though a number of polymeric microfibers have been produced by RESS previously, to our knowledge, this is the first report which demon-

* Corresponding author. Tel.: +82 51 620 6409; fax: +82 51 629 6408.
E-mail address: ktlim@pknu.ac.kr (K.T. Lim).

0896-8446/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2008.05.011

strates the application of supercritical RESOLV method to prepare PAN nanofibers.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, average Mw = 150,000 g/mol) was purchased from Aldrich. Research grade CO_2 (99.99%, Daeyoung Co, Korea) was used as received. Dimethylformamide (DMF, Junsei, Korea) was distilled prior to use.

2.2. Experimental set-up for the preparation of PAN nanofibers by RESOLV

General schematic apparatus for the RESOLV method is shown in Fig. 1. Briefly, the equipment consists of an extraction unit and an expansion unit including high-pressure syringe pump (ISCO 260D) and auxiliary facilities. The main component of the experimental apparatus is a high-pressure cell equipped with a sapphire window secured at one end. Heating was provided by a water bath and the temperature was measured with a thermocouple (Doric Trendicator 400 A). The water bath was controlled with a temperature controller (Jisico model J-IVW8, Korea) and a Teflon-coated magnetic stir bar was used to mix the cell contents in the reactor to obtain a homogeneous solution. A capillary nozzle with a diameter of 150 μm and length of 10 mm was adapted as the expansion device. In a typical experiment, 2–6 mg of PAN in 4 mL of CO_2-DMF (25%, v/v) solution was pressurized by the syringe pump and the reactor was then immersed in a water bath to attain required supercritical condition. The pre-expansion temperature and pressure were maintained at 60 °C and 20.7 MPa, respectively, for this study. After an hour of equilibrium, the solution was rapidly depressurized and the expanded solution was passed through the capillary nozzle into a chamber containing ambient water in which PAN is insoluble. The PAN nanofibers obtained in the aqueous suspensions were collected on glass slides for further characterization.

2.3. Carbonization of PAN nanofibers

For carbonization, the PAN fibers produced by the RESOLV were placed in a tube furnace and stabilized in air for 1 h at 300 °C followed by carbonization at 800 °C for 4 h under N_2 atmosphere.

2.4. Characterization

The morphologies of the PAN nanofibers produced by RESOLV were analyzed by field emission scanning electron microscopy (FESEM, Hitachi JEOL-JSM-6700F). The specimen for FESEM imaging was prepared by depositing a few drops of diluted nanofibers aqueous suspensions onto a glass slide followed by drying under ambient conditions. The thermal properties of PAN nanofibers and their carbonized derivatives were analyzed on a PerkinElmer Pyris-I TGA analyzer, at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Preparation of PAN nanofibers by RESOLV

In general, both the RESS and RESOLV methods require a good solubility of polymeric materials in $scCO_2$. Thus, so for, most of the $scCO_2$ expansion studies were devoted to fluorinated polymers which are known to be highly soluble in CO_2 [12]. However, recent studies have shown that the RESOLV can also be extended to polymers which are insoluble or show negligible solubility in CO_2 [17]. For example, polymeric nanoparticles and nanofibers of poly (methyl methacrylate) and a biodegradable polymer poly (lactic acid) were produced by utilizing methanol as the cosolvent with $scCO_2$ [18]. Since the solubility of PAN in CO_2 is negligible, DMF was selected as the cosolvent in this study.

Before performing RESOLV experiments, the solubility behavior of PAN in DMF-$scCO_2$ cosolvent system was studied. To obtain a clear and homogenous $scCO_2$ phase, it was found that, for 6 mg of PAN in 4 mL CO_2 at least 25% (v/v) of DMF (with respect to $scCO_2$) is required at the pressure and temperature of 20.7 MPa and 60 °C, respectively. These conditions were fixed as the pre-expansion temperature and pressure in this RESOLV study. In a typical RESOLV experiment, a solution of 2 mg of PAN in 1 mL DMF in a 4 mL high-pressure reactor was pressurized with CO_2 by using a syringe pump and then the cell was immersed in water bath to reach the desired supercritical temperature (60 °C). After an hour of equilibrium, the solution was rapidly depressurized at 20.7 MPa and the expanded solution was passed through the capillary nozzle into a chamber containing ambient water instead of ambient air, as found in traditional RESS experiments. The expansion flow rate of CO_2 was maintained at 1–3 mL/min. Since the PAN is insoluble in water, it started to precipitate in the form of nanoparticles, initially. The expansion of supercritical solution took about 10 min. In the first 5 min of the rapid expansion, the aqueous suspension

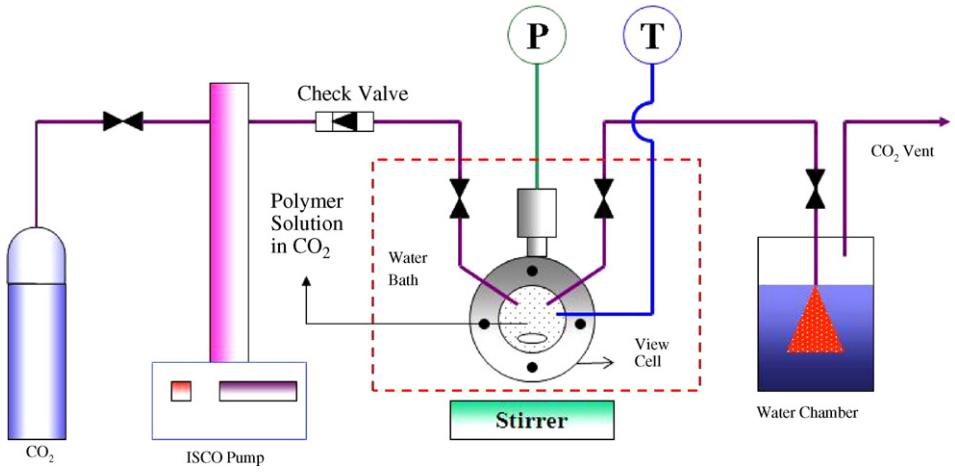

Fig. 1. Experimental setup for the preparation of PAN nanofibers by RESOLV.