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Synthesis and characterization of a water-soluble nylon copolyamide

Yongping Bai [a], Lei Huang [a], Tong Huang [a], Jun Long [a,*], Yongfeng Zhou [b,*]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China
[b] School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composite, Shanghai Jiao Tong University, Shanghai 200240, PR China

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ABSTRACT

A novel water-soluble copolyamide based on Nylon 66 was synthesized via solution-melt polycondensation of hexanedioic acid and sodium 5-sulfoisophthalate with 1,6-diaminohexane. The chemical structures of the products were ascertained by various spectroscopic techniques (FT-IR, Raman, and ^{1}H NMR). The thermal properties of the polyamides under consideration were measured by TGA and DSC. According to the temperature dependence of FTIR spectra, it was found that the average strength of the intermolecular hydrogen bond of the water-soluble copolyamides becomes weak with increasing the temperature. It was found that the obtained random copolyamides could self-assemble into spherical micelles in aqueous solution with the size dependent on the hydrophilic fraction according to the DLS and TEM measurements.

1. Introduction

Polyamides are strong and important engineering materials, and have been widely applied in industry and investigated in scientific field due to their excellent properties such as good chemical resistance, abrasive resistance and good toughness etc [1–8]. However, traditional organic solvent-soluble polyamides will release volatile organic compounds (VOC) in actual applications, which can pollute air and do harm to human health. With the rapid development of eco-friendly materials and the increase of human environment protection consciousness, polyamides should be either high-performance or renewable. Water-soluble polyamides can meet this challenge. They possess excellent properties such as good toughness, corrosion resistance and good temperature resistance etc. and what's more, they also possess outstanding environmental advantages such as non-toxicity, incombustibility and good biocompatibility etc. Such prominent properties have encouraged in pursuit of novel water-soluble polyamides for applications in areas such as packaging materials [9], water-based coating [10] and drug carrier [11] etc.

As a consequence, water-based polyamides [12–15] have attracted much attention in recent years. Many people have made significant efforts to increase the water solubility of polyamides by chemical modification. Neuse and Perlwitz et al. synthesized a series of water-soluble aliphatic polyamides from polysuccinimide by nucleophilic ring opening, which possessed intrachain-type or side chain-attached, primary or secondary amine functions capable of drug binding [16–18]. Subsequently, in their ongoing research Neuse et al. prepared various waterborne polyamides as drug carriers, which contained hydrosolubilizing chains or groups such as carboxyl groups [19–21], poly(alkylene oxide) chain segments [22,23], hydroxyethyl [24]. Ueda et al. reported a rapid, inexpensive and highly efficient convergent synthesis of 32-amine-terminated polyamide dendrimer by the hydrolysis of trifluoroacetamide groups. Then the resulting dendrimer could be successfully modified with oligo (ethylene glycol) chains at its periphery to afford a novel water-soluble polyamide dendrimer [25]. Araki et al. prepared a water-soluble polyamide carrying $-NH(CH_2CH_2NH)_5-$ segments in the main chain, and these polyamides show polyelectrolyte behavior in aqueous solution [26]. Maslyuk et al. synthesized a series of light-sensitive water-soluble copolyamides with terminal carboxyl, amine, and photoinitiating (benzoin) fragments in the macro-chain via polycondensational telomerization of a mixture of ethylene diglycol, piperazine, adipic acid and hexamethylenediamine at various benzoin concentrations. They also investigated the change in intrinsic viscosity during synthesis [27].

However, few studies have been performed on the water-soluble modification of commercially available polyamides such as Nylon series [28]. In addition, water soluble polyamides are very promising in drug delivery; however, most of the present work is limited to grafting drugs into the main chains of polyamides to form

* Corresponding authors.
E-mail addresses: longjun@hit.edu.cn (J. Long), yfzhou@sjtu.edu.cn (Y. Zhou).

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drug conjugates [18]. In recent years, self-assembled micelles are widely accepted to encapsulate drugs to realize efficient drug delivery [29–36]. So, if polyamides can self-assemble into micelles in water, the application potentials of them in drug delivery can be greatly extended. Unfortunately, to our knowledge, few works has been done on the self-assembly behavior of water-soluble polyamides due to the lack of amphiphilicity.

In this paper, a series of novel water-soluble copolyamides based on Nylon 6,6 were successfully synthesized by simple step-heating solution-melt polycondensation [37]. Sulfonates were introduced in the backbones to render the polymers water-soluble. The prepared nylon polyamides were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectra (Raman), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, the variations of hydrogen bonds during the heating process were also studied by the temperature-dependent FTIR. The obtained polymers also show a micellization behavior in water according to the transmission electron microscopy (TEM) and dynamic laser light scattering (DLS) measurements. The present work may broaden the scope and application area of polyamides.

2. Experimental part

2.1. Materials

1,6-Diaminohexane (TCI), sodium 5-sulfoisophthalate (NaSIPA, TCI), hexanedioic acid (Acros), sodium hypophosphite (Acros) and anhydrous ethanol (Acros) were used as received.

2.2. Experiments

Water-soluble copolyamide, PA66-co-PA6SIP, were synthesized by means of forming-salts and solution-melt polycondensation as follows (Scheme 1): sodium 5-sulfoisophthalate and was dissolved in deionized water and added slowly into absolute alcohol solution of 1,6-Diaminohexane with vigorously stirring. Hexanedioic acid was dissolved in absolute alcohol and added slowly into absolute alcohol solution of 1,6-Diaminohexane with vigorously stirring. The two white salts were recorded as PA6SIP salt and PA66 salt, respectively. Then PA66 salt was fully precipitated after it was stirred for 30 min. PA6SIP salt was isolated by rotary evaporation, and then was filtered with Buchner funnel and washed with absolute alcohol repeatedly. White powders were obtained after dried in a vacuum oven overnight.

A typical synthesis process of the water-soluble PA66 is shown as follows. Firstly, the obtained PA6SIP and PA66 salts and sodium hypophosphite (0.1%wt) were dissolved in ethanol water. Then the solution was filled into an autoclave. And the autoclave was evacuated and flushed with nitrogen for three times. Subsequently, the autoclave was heated until 180 °C, meanwhile, the pressure was increased to 1.6 Mpa. After 1.5 h, the temperature was raised by 50 °C again and the pressure was gradually decreased to atmospheric pressure in 2 h and the reaction temperature of the autoclave was increased to 270 °C. The autoclave was evacuated to 40 Pa for further polycondensation. Five hours later, the autoclave was cooled to room temperature and the reaction was stopped. Finally, the brown product of PA66-co-PA6SIP was obtained. For simplicity, we denoted it as coPA, and three samples of coPA1-3 were synthesized by changing the feed ratio of PA6SIP and PA66 salts. PA66 was prepared by the similar procedure at different temperatures. The real composition and yield of the obtained polyamides were listed in Table 1.

2.3. Characterizations

FTIR measurements were carried out on a Perkin–Elmer Spectrum 100 PC Fourier transform infrared spectrometer, equipped with a high temperature chamber, in the range of 500–4500 cm^{-1} with an accuracy of 4 cm^{-1}. Raman spectra were collected on a Bruker Senterra Raman spectrometer. The Varian Mercury Plus spectrometer was used to obtain ^1H NMR spectra (400 MHz) with sulfuric acid used as solvent. Intrinsic viscosity in sulfuric acid was determined in an Ubbelodhe viscometer at 25 ± 0.1 °C.

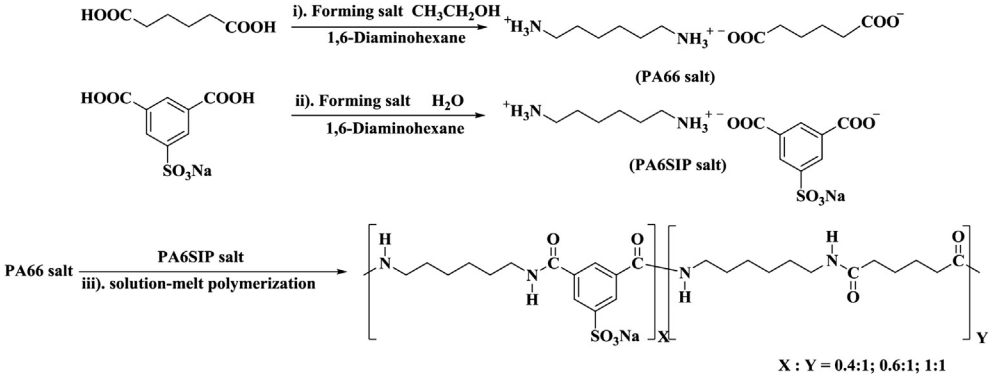
The differential scanning calorimetry (DSC) traces were recorded on a Perkin–Elmer Q2000 differential scanning calorimeter at the rate of 10 °C min^{-1}. The temperature was calibrated with indium. The thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Q5000IR thermobalance with heating rate of 20 °C min^{-1} and nitrogen was used as the purge gas.

Transmission Electron Microscopy (TEM) analysis was performed on a JEM-2100/INCA OXFORD instrument operating at an accelerating voltage of 200 KV. The samples were sprayed onto the carbon-coated copper grids and air-dried at room temperature before measurement. The dynamic light scattering (DLS) measurement was performed in aqueous solution at 25 °C at a scattering angle of 90°, using a Malvern Zetasizer Nano S apparatus equipped with a 4.0 mW laser operating at $\lambda = 633$ nm.

3. Results and discussion

3.1. Chemical characterization of synthesized polyamides

The molecular weight characterization of the obtained coPA samples by GPC is very difficult since the adsorption of the polymers with GPC column is very serious. Instead, the intrinsic



Scheme 1. The synthesis of the water-based copolyamides of PA66-co-PA6SIPs.