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ORIGINAL ARTICLE

Optimization of amine-terminated polyacrylonitrile synthesis and characterization

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Abstract Amine-terminated PANs were prepared in two steps. The first step includes free radical polymerization of acrylonitrile (AN) using initiator pair of ammonium persulfate and sodium thio-sulfate as redox system. In the second step, the amino groups were introduced through the reaction of polyacrylonitrile with excess of different diamines (10-fold) including ethylenediamine (EDA), hexamethylenediamine (HMDA) and octamethylenediamine (OMDA), to yield PAN-EDA, PAN-HMDA and PAN-OMDA, respectively. Optimization of the amine-terminated PANs synthesis was carried out at different temperatures (30–90 °C) and different time intervals (4–24 h). In addition, the introduction of the amino group was followed by the piperidine test and recording of the FT-IR spectra. All polymers were characterized by, ¹H NMR spectra, thermogravimetric analysis (TGA), and FT-IR spectra.

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1. Introduction

Chemical reactions of polymers have received much attention in which several fundamentally functionalized polymers were prepared by the reaction of linear or crosslinked polymers and by the introduction of reactive polymer chains (Horie

et al., 2003). Considerable interest has been focused on functional polymers and on their diverse applications in many fields such as biomedical applications including drug delivery and antimicrobial polymers. Functional polymers have potential advantages over small analogue molecules. Their usefulness is related to both the functional groups and to their polymeric nature whose characteristic properties depend on the extraordinarily large size of the molecules (Kenawy et al., 1998; Akelah and Moet, 1990).

Polyacrylonitrile (PAN) is an important polymer which has many desirable properties like solvent resistance, abrasion resistance, thermal and mechanical stability, high tensile strength and possesses good insect resistance (Jain et al., 2009). Polyacrylonitrile finds many applications in the areas of composites, protective clothing, nanosensors, gas separation technology and in biochemical product purification and for

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biomedical applications (Jain et al., 2009). Active nitrile groups present in polyacrylonitrile allow for the introduction of new functional groups by special reactions. Among the reactions of the nitrile group modification are the hydrolysis and reduction to produce carboxyl and amine functionalities, respectively (Kiani et al., 2011). In recent years, there has been much interest in synthetic polymeric fibers suitable for medical applications. Anirudhan and Ramachandran (2008), Kiani et al. (2011) have reported different methods of modifications of polyacrylonitrile fibers to obtain cationite, anionite, and ampholyte. Some authors carried out surface modifications of polyacrylonitrile with sodium hydroxide to obtain a significant number of carboxylic groups (Kiani et al., 2011; Bilba et al., 2006) and others have applied modification with hydroxylamine to form hydroxy-functionalized resins (Anirudhan and Ramachandran, 2008; Kiani and Arsalani, 2006; Arsalani and Hosseinzadeh, 2004; Arsalani et al., 2009). Amine functionality on the surface of polyacrylonitrile fibers was introduced by reduction with lithium aluminum hydride (Jain et al., 2009). Recently, aminated polyacrylonitrile fibers have been used for the removal of metal ions such as chromium, copper, and lead, but with low metal sorption capacity (Arsalani et al., 2009; Deng and Bai, 2004; Deng et al., 2003; Bagheri et al., 2010). Also, Lin et al. synthesized polyacrylonitrile fiber-supported palladium catalyst which was used in Heck reactions (Arsalani et al., 2009; Lin et al., 2003).

The objective of the present study was to prepare amine-terminated polymers as functional polymers for use in biomedical applications. The synthesis of amine-terminated polyacrylonitrile was carried out by the reaction of polyacrylonitrile with different types of diamines at different time intervals and different temperatures to reach the optimum conditions.

2. Experimental

2.1. Materials

Acrylonitrile (AN) was purchased from Loba Chemie, Spain. Ethylenediamine (EDA), hexamethylenediamine (HMDA) and octamethylenediamine (OMDA) were purchased from across. Bromophenol blue (BPB) was purchased from PRO-LABO. Piperidine was purchased from BDH Chemicals Ltd Poole England. All solvents were used as received without further purification.

2.2. Characterization techniques

^1H NMR spectra were recorded on a JEOL JNM-PM X90 Si-NMR spectroscopy instrument. Thermal properties were

examined by using thermogravimetric analysis (TGA) which was carried on TA-Q500 System of TA; samples of 5–10 mg were heated in the temperature range of 30–800 °C at a scanning rate of 10 °C min⁻¹ under nitrogen atmosphere. Fourier-transformer infrared (FT-IR) Spectra were recorded using TENSOR 27, Bruker. UV Spectra was recorded using Perkin-Elmer Lambda 35 UV-vis spectrophotometer.

2.3. Polymer synthesis

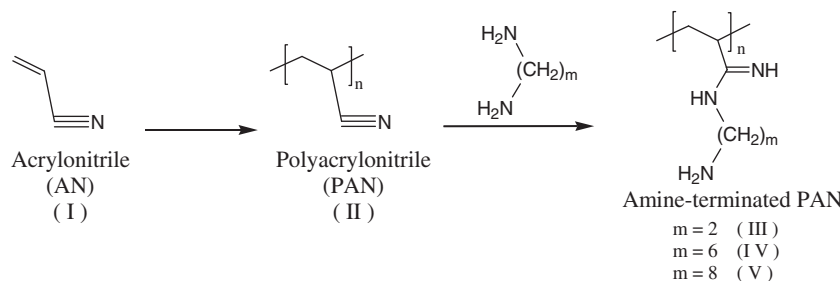
Polyacrylonitrile PAN (II) was prepared by precipitation polymerization using a redox initiation system in aqueous solution according to the procedure by Braun et al. (2005). The procedure can be summarized as following; In a 250 mL round-bottomed flask, acrylonitrile (AN) (I) (15 mL, 230.3 mmol) was mixed with distilled water (175 mL) at room temperature with stirring under nitrogen atmosphere. Then, sodium disulfite solution (5%, 0.5 mL, 0.13 mmol) and ferrous sulfate solution (2.5 mL, 9.10 mmol), were added followed by potassium peroxydisulfate solution (5%, 2.5 mL, 0.46 mmol). The turbidity was noted after 5 min and stirring was continuing for more than 20 min. The precipitated polymer (II) was filtered and was washed with distilled water (300 mL) and finally with methanol (100 mL). The product PAN (II) was dried in a vacuum oven at 50 °C overnight to yield 8.3 g (55% yields). The ^1H NMR spectrum (400 MHz, DMSO-*d*₆, ppm, Si(CH₃)₄) of PAN (II) showed peaks at: δ 2.03 ppm (singlet, g, $-\underline{\text{C}}\underline{\text{H}}_2-\text{CH}-$), δ 2.13 ppm (triplet, $-\text{CH}_2-\underline{\text{C}}\underline{\text{H}}-$).

2.4. Synthesis of amine-terminated polyacrylonitrile PANs (III–V)

2.4.1. General procedure

In a 100 mL round-bottomed flask, to an excess of the diamine (10-fold) in absolute ethanol (60 mL), Polyacrylonitrile (II) (1.0 g, 17.9 mmol) was added portionwise over 1 h with stirring under nitrogen. The reaction mixture was stirred for 1–2 h at room temperature and at 70 °C for 12 h. The product was filtered, washed with methanol (60 mL) and was dried in an oven under vacuum at 40 °C overnight. The following quantities were used:

2.4.1.1. Polyacrylonitrile-terminated ethylenediamine PAN-EDA (III). EDA (126 mL, 113.2 g, 1883 mmol), and PAN (II) (10 g, 179 mmol) to yield 12.2 g (57% yield). The ^1H NMR Spectrum showed peaks at: δ 1.21 ppm (1H, $-\text{CH}_2-\underline{\text{C}}\underline{\text{H}}-$), δ 2.15 ppm (2H, $-\underline{\text{C}}\underline{\text{H}}_2\text{CH}-$), at δ 2.04 ppm (1H, $=\underline{\text{N}}\underline{\text{H}}$), δ 2.09 ppm (1H, $-\text{CN}\underline{\text{H}}\text{CH}_2-$), δ 2.11 ppm (2H, $-$



Scheme 1 Redox polymerization of acrylonitrile and synthesis of amine-terminated PANs.

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