

One-pot low temperature synthesis and characterization of hybrid poly(2-pyrrolidone) microparticles suitable for protein immobilization

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ABSTRACT

Neat and hybrid poly(2-pyrrolidone), i.e. polyamide 4 (PA4) microparticles containing magnetic or conductive metal, metal oxide, or carbon nanotube fillers were prepared via environmentally-friendly solventless activated ring-opening polymerization of 2-pyrrolidone at 40 °C. The method produces high porosity microparticles with diameters of 5–12 μm and conversion to PA4 of 56–65%. Their structure and properties were characterized by light- and electron microscopy, thermal, spectral and X-ray diffraction techniques. Two crystalline polymorphs, namely α - and β -PA4, were found to coexist at room temperature by X-ray diffraction. The assessment of the adsorption capacity of the PA4 hybrid microparticles toward model protein showed up to 60% efficiency only after 1 h of incubation without any preliminary activation or functionalization.

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1. Introduction

The synthesis of Nylon 4 or polyamide 4 (PA4) by ring-opening bulk polymerization of 2-pyrrolidone (2PD) was first patented by Ney et al., in 1953 [1], followed by some improvements disclosed by C. Barns [2]. Later theoretical studies showed that a non-activated anionic polymerization of 2PD takes place under those conditions initiated by the in-situ forming of alkali salt of 2PD, e.g., 2-oxo-1-pyrrolidinyl potassium [3]. Sekigichi et al. [4] used N-acetyl lactams as activators of the anionic polymerization of 2PD and its derivatives, the anionic initiator being pre-prepared alkaline salts of lactams or such with non-metallic cation. Another activator specific for the 2PD polymerization obtained in-situ as a reaction product of 2PD-alkali salt and benzoyl chloride has been described by Kawasaki et al. [5]. Similar initiator-activator system and reaction conditions were applied more recently to synthesize high molecular weight anionic PA4 homopolymer and PA46 copolymers [6].

Soon after the first successful syntheses it was established that, because of its high amide content, PA4 demonstrates mechanical resistance, dyeability and moisture intake significantly higher than

the traditional polyamides for textile fibers. However, the dense network of intermolecular H-bonds between the backbone amide groups results in a high melting temperature of ca. 265 °C at which fast and intense thermal degradation starts. This impedes the normal melt processing of PA4 to filaments, whereas the solution spinning alternative has shown prohibitive costs [7]. Efforts for improving the thermal stability of PA4 have been attempted by either chemical modification of chain ends [8,9] or backbone amide groups [10], even though only marginal improvements have been reported. All this resulted in low interest toward PA4 in the form of textile fibers.

During the last decade, however, the relatively easy degradation of PA4 and its possible practical implementation have been subject of intensive research. The thermal degradation of PA4 is considered to occur by a depolymerization mechanism based on the low thermodynamic polymerizability of 2PD [11,12]. Moreover, PA4 and some of its copolymers have been reported to be biodegradable in compost soils and activated sludge, containing certain bacteria and fungi [13,14], as well as in seawater [15]. At the same time, some very recent studies indicate that the 2PD monomer can be prepared from biomass by a hybrid synthetic route involving biological and chemical processes [16].

The biodegradability of PA4 in various environments and the possibility of sustainable synthesis of the 2PD monomer could potentially result in interesting biotechnological applications thus

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reestablishing the industrial interest toward products on its basis. For this to happen, it is of prime importance to find a way to produce PA4 directly in its form of application, e.g., particles with controllable structure and morphology, without the use of melt processing or such including toxic and polluting solvents. As a step in this direction, Kim et al. [17] developed a process for PA4 microspheres prepared by activated anionic ring-opening polymerization (AAROP) of 2PD in a paraffin oil/2PD heterogeneous medium, in the presence of suitable surfactant. Potassium tert-butoxide and benzoyl chloride were used for in-situ preparation of the initiator/activator complex.

The present work suggests a simplified and environmental-friendly method based on AAROP of 2PD to produce PA4 microparticles in good yields, with controlled size, shape and porosity. The polymerization occurs at mild conditions of 40 °C and uses the proper 2PD monomer as a reaction media thus excluding any solvents or surfactants. Both neat PA4 microparticles (MP) and hybrid PA4 microparticles (HMP) carrying loads of magnetic or conductive micro- and nanofillers were synthesized. To the best of our knowledge, one-pot synthesis of hybrid PA4 microparticles with magnetic or electro conductive loads has never been reported before. The structure, morphology and the most important properties of the MP and HMP were characterized. A preliminary study on their adsorption capacity toward a model protein was also carried out.

2. Experimental

2.1. Materials

2-Pyrrolidone 99%, (2PD) was purchased from Sigma Aldrich and used as received. As polymerization activator, Brüggolen C20[®] (C20) from Brüggemann Chemical, Germany was used. According to the manufacturer, it contains 80 wt % of blocked aliphatic diisocyanate in ECL (Fig. 1, C20). The initiator sodium dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (80 wt % in toluene) (Dilactamate[®], DL) was purchased from Katchem and used without further treatment (Fig. 1, DL).

The powdered Fe₃O₄ and Cu are products of Sigma-Aldrich with +99% purity and grain sizes of 50–80 nm and >10 μm, respectively. The soft, non-insulated Fe particles (99%) with average diameters of 3–5 μm were kindly donated by the manufacturer BASF, Ludwigshafen. Two types of such Fe particles were used – without and with phosphate coating. The multi-walled carbon nanotubes (CNT) were purchased from Sigma Aldrich. The acetone and methanol solvents of “puriss” grade were purchased from Sigma-Aldrich and used as received.

2.2. Anionic ring opening polymerization to microparticles

The polymerization was carried out in a 250 mL glass flask

supplied with magnetic stirrer and inlet for dry nitrogen. In a typical synthesis of neat PA4 microparticles (PA4 MP), 0.2 mol of 2PD and 1.5 mol % of C20 were added and stirred until the latter reagent was fully dissolved. Then, 3 mol % of DL were added under nitrogen atmosphere. The temperature was gradually increased from 23 °C to 40 °C and the system was put under 50 mbar. Reaction times of 6 and 24 h (from the point of DL addition) were applied for all samples, the temperature being kept at 40 °C under constant stirring. The PA4 MP fine powders were isolated by dissolving the reaction mixture in acetone in order to eliminate the non-polymerized 2PD, followed by vacuum filtration, washing several times with methanol to eliminate low molecular weight oligomers and drying the product for 1 h in a vacuum oven at 50 °C. All PA4 powders were then subjected to a 4 h Soxhlet extraction with methanol to eliminate any traces of oligomers.

In a typical synthesis of hybrid PA4 HMP, 1 wt. % of the filler (Fe with or without phosphate coating, Cu, Fe₃O₄), or 0.1 wt. % of CNT was added to 2PD prior the catalytic system, under nitrogen and stirring. The rest of the polymerization and isolation procedures were performed in the same way as in the case of PA4 MP. Table 1 presents the sample designation and compositions.

2.3. Experimental methods

The intrinsic viscosity measurements were performed with neat PA4 particles in 97% sulfuric acid at a concentration of 0.2 g/dL with a suspended level Ubbelohde viscometer thermostatted at 23 °C. Flow times are recorded as an average of at least 10 runs.

Bright field optical microscopy of PA4 particles' sizes, roundness, and their distributions were performed in an Olympus BH-2 microscope (Japan) equipped with the Leica Application Suite 4.4 software for image processing. The scanning electron microscopy (SEM) studies were performed in a NanoSEM-200 apparatus of FEI Nova using mixed secondary electron/back-scattered electron in-lens detection. The pulverulent samples were observed after sputter-coating with Au/Pd alloy in a 208 HR equipment of Cressington Scientific Instruments with high-resolution thickness control.

The differential scanning calorimetry (DSC) measurements were carried out in a 200 F3 equipment of Netzsch at a heating/cooling rate of 10 °C/min under nitrogen purge. The typical sample weights were in the 10–15 mg range. The thermal stability and the real inorganic load RL of all PA4 powders were established by means of thermogravimetric analysis (TGA) in a Q500 gravimetric balance (TA Instruments), heating the samples to 600 °C at 10 °C/min in a nitrogen atmosphere. The RL value of PA4 HMP was calculated according to Equation (1):

$$RL = R_i - R_{PA4}, \quad [\%] \quad (1)$$

where R_{PA4} is the carbonized residue at 600 °C of neat PA4 particles

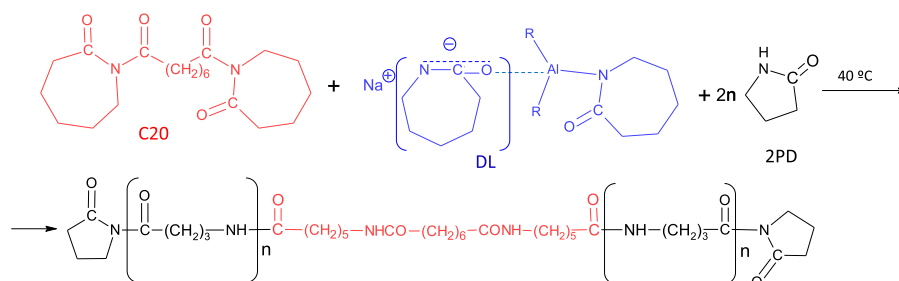


Fig. 1. Chemical reactions occurring during AAROP of 2PD to microparticles: C20 – chemical structure of the active substance of the C20 activator; DL – chemical structure of dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (initiator), R = OCH₂CH₂OCH₃; 2PD = 2-pyrrolidone.

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