



High crystalline, porous polyamide 6 by anionic polymerization

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ABSTRACT

Polyamide 6 (PA6), also known as Nylon 6 is a widely used industrial polymer. The structural properties of PA6 play an important role in its potential commercial applications. We report that the anionic polymerization of ϵ -caprolactam in the presence of liquid additives such as o-Xylene, m-Xylene, p-Xylene and toluene at a critical concentration led to the formation of high crystalline, porous polyamide 6 (aPA6). Porous aPA6 samples possess hierarchical spherulitic morphology where 10 μm size spherulitic granules are interconnected by submicron size fibrillated domains. The size and shape of spherulitic domains change with the type of liquid additives used during the synthesis of porous aPA6. The presence of liquid additives influences the kinetics of the exothermal processes during polymerization, which ultimately leads to a solid-liquid phase separation prior to the formation of porous networks of spherulites. Such process also leads to thickening of lamella and formation of second order crystals that contributed to highest crystallinity in porous aPA6 ever reported. Differential scanning calorimetric along with wide-angle X-ray scattering study reveal ~60% crystallinity in all porous aPA6, which is about 60% increase in comparison with the neat aPA6 (~40%). Higher crystallinity in porous aPA6 also exhibited 50% reduction in moisture uptake in comparison with the neat aPA6.

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1. Introduction

Polyamides are hydrogen-bonded polymers where the crystal structures are defined by the arrangement of hydrogen bonding among amide groups. The weight or volume fraction of different crystal structures plays critical role in determining some important physical properties such as toughness and water absorption of polyamides. Thus, the engineering of crystal structures and modulation of crystallinity is important to tune the physical properties of polyamides for desired applications. Polyamide 6 (PA6), also known as Nylon 6, is widely known for their high impact resistance, good toughness, abrasion resistance and strength. The crystallinity and crystal structure play important role in improving the physical properties of PA6. The structure of PA6 is mainly defined by the organization of chains in 2D hydrogen-bonded sheets that are held together by van der Waals interactions in a 3D lattice. To date, four

monoclinic crystal phases of PA6 have been reported in the literature: α , α' , β , and γ , where α is thermodynamically stable phase and γ is kinetically favored [1–6]. In addition, the chain axis-repeat length for the α form is 17.2 Å and 16.8 Å for the γ form [7,8]. This chain axis-repeat significantly affects the strength of hydrogen bonding and collectively to the strength of PA6 [1,7,8]. Thus, the weight fraction of each of these crystal phases, determines the toughness and stiffness of PA6. The percent crystallinity of PA6 depends on the crystallization condition, filler/additive kinds and contents, and most importantly the synthetic protocol to produce them.

Commercially, PA6 is synthesized by the ring-opening polymerization of ϵ -caprolactam by hydrolysis (hPA6). This hydrolytic polymerization process is more industrially viable because it is easier to control and better adapted for large-scale operation [1,11]. However, the production of hPA6 involves multiple steps such as: ϵ -caprolactam and additive addition, hydrolysis, condensation, pelletizing, leaching/extraction of monomers, drying, and packaging. In order to reduce such multiple steps, a single pot synthesis of PA6 was necessary for effective injection molding of PA6. Due to

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the fast reaction kinetics, clean polymerization reaction without any by-products and a crystalline end-product is a challenge. Anionic ring-opening polymerization of lactams is a one pot synthetic route for PA6 that has been extensively studied by Sebenda, Sekiguchi, Wichterle, Gabbert, Hendrick and many others followed their studies [9–17]. Anionically polymerized polyamide 6 (aPA6) exhibits similar properties like conventional hydrolytically polymerized PA6 (hPA6). However, the crystallinity of aPA6 (~40%) is higher than the hPA6 (~30%) because aPA6 is synthesized at 150 °C (close to the crystallization temperature of PA6) whereas hPA6 is synthesized at 230 °C (above the melting point of PA6). Thus, aPA6 exhibits better toughness and impact resistance over hPA6. Stebbins et al. conducted a detail study on the effect of polymerization temperature, initiator concentration and annealing condition on the crystallinity [18–20]. Stebbins et al. showed that maximum crystallinity of 44% can be achieved when the polymerization was done at 150 °C [18]. The crystallinity and percent yield decreases above and below this temperature.

Anionic ring opening polymerization of lactams, with some modification, has been reported to produce crystalline particles of aPA6 (crystallinity, 30% to 40%) which are very convenient for many processing procedures, such as: flame spraying, electrostatic coating, pastes production, dispersions, and lacquer binders [21–26]. Moreover, they also possess good adsorption properties due to their extended porous, spherulitic surface morphology [25,26]. Dan et al. reported the synthesis of aPA6 crystalline granules by utilizing anionic polymerization of ϵ -caprolactam in ethylbenzene solvent where molten ϵ -caprolactam and a non-solvent hydrocarbon mixture [27]. They proposed that the formation mechanism of crystalline granules of aPA6 involved three steps; i) the liquid medium (solvent) facilitates the transport of monomer and catalytic system to the growing macromolecules, ii) monomers grow faster in the homogeneous liquid phase, iii) as the macromolecules grow, the medium becomes a poor solvent for ϵ -caprolactam which favors a rapid precipitation of chains and forms aggregates at higher concentration [27]. These aggregates hinder the diffusion of ϵ -caprolactam anion to macromolecules and thus stop the polymerization, which result in porous, spherulitic granules of aPA6, not a continuous porous film. Dan et al. also studied the effect of different catalytic systems and initiators on the morphology of such spherulitic crystalline granules of aPA6. ²⁷The crystallinity of such granules were around 40%, which includes the contribution from both α , and γ crystal phases as the X-ray studies indicated. Such study gives an important indication that the polymerization of ϵ -caprolactam in a non-reacting liquid medium could be utilized to control the fabrication of high crystalline porous aPA6. This contribution presents a systematic study, for the first time, to produce highly crystalline (>50%) porous aPA6 by anionic polymerization of ϵ -caprolactam with a non-reacting liquid medium. Such high crystalline porous aPA6 may have potential applications as ultra/microfiltration membranes, high specific strength materials, sintering powders for 3D printing, low viscosity additive for commercial polyamides, and/or high volume throughput tubing.

It is important to mention here that, there are other methods such as immersion/precipitation or interfacial polymerization, which have been used to produce porous membranes of different polyamides having similar spherulitic structures [28–33]. This paper reports a one pot synthesis of porous aPA6 with very high crystallinity and open porosity. Detailed experiments have been carried out to investigate the mechanism of formation of such high crystallinity, porous aPA6. Detail X-ray scattering studies have been carried out to better understand the crystal structures and crystallinity.

2. Experimental section

Materials. Monomer ϵ -Caprolactam, catalyst Brüggolen C10 (Sodium Caprolactamate) and initiator Brüggolen C20 (Bifunctional hexamethylene-1,6-dicarbamoylcaprolactam) were supplied by BASF, Germany. Four different liquid additives: Toluene, o-Xylene, m-Xylene and p-Xylene were used to synthesize porous, crystalline aPA6 by anionic polymerization. All liquid additives were purchased from Alfa Aesar and used as received. Relevant physical properties of each liquid additives are reported in Table S1.

Synthesis of solid and porous aPA6. Anionic polymerization of ϵ -Caprolactam was carried out in a 20 ml glass vial under atmospheric pressure. Monomer ϵ -Caprolactam and initiator C20 were melted and mixed at 150 °C under constant stirring. Polymerization takes place as soon as the catalyst C10 was added to monomer and initiator mixture. In order to synthesize the porous aPA6, liquid additives were added to the monomer and initiator mixture before adding the catalyst. The formulation of monomer, initiator, additives and catalyst is shown in Table 1. Figure S1 reports the chemical structures of monomer, catalyst and initiator used in this study. In addition, Figure S1b shows the reaction scheme for the synthesis of aPA6 by anionic polymerization and Figure S1c shows a generalized sketch of the steps involved in synthesizing porous aPA6.

Morphology of porous aPA6. Morphology investigation of porous aPA6 was carried out on the surface and cross-section of cryofractured samples by using a scanning electron microscope (SEM). Samples were sputter-coated with gold prior to imaging. In order to characterize the open porous morphology of porous aPA6, a simple filtration test was carried out using a dead-end filtration setup. Coffee suspension was filtrated through a 1 mm thick porous aPA6 and the filtrates were characterized by SEM after filtration.

Density and porosity of porous aPA6. The porosity was determined using a density method as defined in the following equation:

$$\text{Porosity} = \left(1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{polymer}}} \right) \times 100\% \quad (2)$$

The bulk density ρ_{bulk} was calculated from the weight and volume of porous aPA6, whereas the volume was calculated from the sample's diameter and thickness.

Differential Scanning Calorimetry. A Differential scanning calorimeter (TA DSC Q200) was used to characterize the thermal transitions and crystallinity of control and porous aPA6 samples. The samples having a size of 4.5 ± 0.1 mg were tested at a heating rate of 10 °C/min in a temperature range of -20 to 250 °C. The samples were hermetically sealed in an aluminum pan prior to testing. The crystallinity of porous aPA6 was calculated using the following equation:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_c} \times 100 \quad (3)$$

Where, ΔH_c for 100% crystalline PA6 is 188 J/g. [34,35]

X-ray Scattering. X-ray scattering was performed using Ganesha SAXS-Lab instrument using Cu k-alpha radiation (0.154 nm). Measurements were made at two sample-detector distances, ~101 mm (wide-angle X-ray scattering, WAXS) and ~441 mm (mid-angle X-ray scattering, MAXS). Percent crystallinity (X_c) was calculated by using the Reflex Module in Accelrys Materials Studio. First, the crystalline and non-crystalline contribution to the total scattering are separated by background estimation method described by Brükner [36]. Next, the non-crystalline contribution is separated in to amorphous and background scattering

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