



Preparation of polyamic acid and polyimide nanoparticles by compressed fluid antisolvent and thermal imidization



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ABSTRACT

Polyamic acid (PAA) nanoparticles were generated by injection of an *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved PAA into a high-pressure CO₂ chamber in which the precipitation of PAA occurred by the antisolvent technique. Supercritical CO₂ was then continuously fed into the chamber to dry the precipitated PAA. The effects of temperature, pressure and PAA concentration on PAA nanoparticle morphology and size were systematically examined. The results indicated that PAA size could be reduced by decreasing temperature or concentration and by increasing pressure. Spherical PAA nanoparticles with reduced coalescence could be generated at the condition of 313 K, 13.79 MPa and 1.0 wt% PAA in NMP. The resultant PAA nanoparticles and the corresponding polyimide (PI) nanoparticles obtained by thermal imidization treatment of PAA at the determined heating conditions were characterized by thermogravimetric analysis and Fourier transform infrared spectroscopy. With evidence of an imide ring structure and high thermal stability, PI was verified to be successfully produced.

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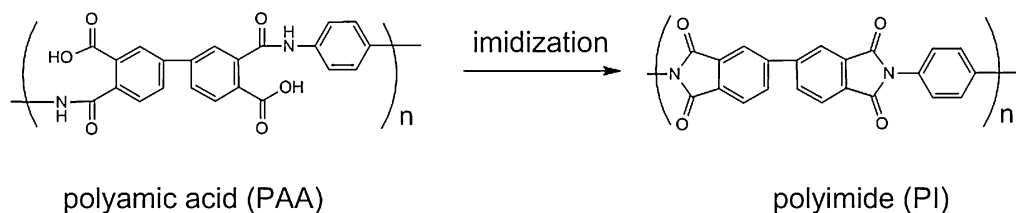
1. Introduction

Polyimide (PI) is considered to be a super engineering plastic due to its high mechanical durability, thermal stability, chemical compatibility and electrical resistivity. Due to these unique properties, PI is widely utilized in microelectronics applications, including high-temperature adhesives, flexible printed circuit boards and passivation layers in semiconductors. Recently, spherical PI nanoparticles have drawn much attention due to their potential as next generation materials, such as nanoreactors, nanofillers, drug delivery carriers and ultralow- k materials [1–9]. Several approaches, including polycondensation [1,2], precipitation [3–6], emulsification [7], electrospraying [8] and ultrasound enhanced titration techniques [9,10], have been proposed for fabricating PI nanoparticles. For example, in the precipitation method, a solvent (e.g., dimethylacetamide) in which PAA is soluble is utilized to form a microemulsion, and then another solvent (e.g., *n*-hexane) is used as antisolvent [3]. Though an organic solvent is required to dissolve PAA prior to PI nanoparticle formation, the use of an organic antisolvent is not considered to be green technology.

Precipitation with a compressed fluid antisolvent (PCA) is a technique used to micronize compounds such as polymers, pharmaceuticals, pigments and explosives, and it has received

wide-spread attention in the recent years [11–19]. In this operation, the dissolution of antisolvent into a solution weakens the interaction between the solvent and solute, thereby causing precipitation of the solute. Generally, PCA can be divided into two categories, supercritical fluid antisolvents (SAS) and pressurized gas antisolvents (GAS), depending on the status of antisolvent. In 1992, Gallagher et al. [11] first proposed using CO₂ as an antisolvent in GAS to recrystallize the explosive, cyclotrimethylenetrinitramine (RDX). They found a strong relationship between the supersaturation ratio and the particle size of RDX, which provided a basis for further research. Later, Dixon and Johnston [12] utilized compressed CO₂ in PCA to generate polystyrene (PS) microspheres. Their results showed that when CO₂ density was 0.7 g/cm³, an increase in temperature resulted in increased particle sizes, from 100 nm to 20 μm. Moreover, the morphology of PS could be changed from microspheres to expanded fibers when the PS concentration was increased from 1 to 5 wt%. Reverchon's group also proposed two controlling mechanisms for PCA micronization, jet breakup and gas mixing [13]. For GAS, jet breakup dominates and results in microparticle formation. In contrast, for SAS, gas mixing is the major mechanism for nanoparticle formation. Chang et al. [14] also demonstrated the precipitation of α-chymotrypsin by SAS in several different phase regions. They employed mathematical modeling to estimate the mole fraction of CO₂ in the mixture and found that the phase behavior of mixtures strongly relates to resultant particle morphology. More cases of particle formation by using PCA technique can be found in the existing reviews [15–19].

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Scheme 1. Chemical structure of PAA and PI.

Recently, our group applied 1,1,1,2-tetrafluoroethane (HFC-134a) and CO₂ as antisolvents in GAS to precipitate cycloolefin copolymer (COC), poly(methyl methacrylate) (PMMA) and PS/PMMA blended polymers [20–22]. Less coalescence of precipitated submicron-sized polymer particles could be achieved when vapor and liquid coexisted in the precipitator. Our results suggested that nucleation primarily occurred in the vapor phase and growth occurred in the liquid phase. In the present study, nanometer-sized PI particles formation was achieved using PCA. As PI is not soluble in most organic solvents, the micronization of its precursor PAA was carried out first. This process was achieved by introducing the antisolvent, compressed CO₂, into an *N*-methyl-2-pyrrolidone (NMP) solution with dissolved PAA to induce precipitation. Several operation variables, including temperature, pressure and PAA concentration in the NMP

solution, were systematically studied. After precipitation, PAA was converted to PI via a thermal imidization process. The resultant PI was verified with the present structure of imide ring and high thermal stability. To the best of our knowledge, the manufacture of PAA and PI nanoparticles using PCA has not been reported before. In addition, this work represents the first time that a thermoset polymer was micronized by the proposed means.

2. Experimental

2.1. Chemicals and materials

The NMP solution containing 16 wt% PAA gel was purchased from UBE Industries, Ltd. (Japan). The main chains of PAA were consisted of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)

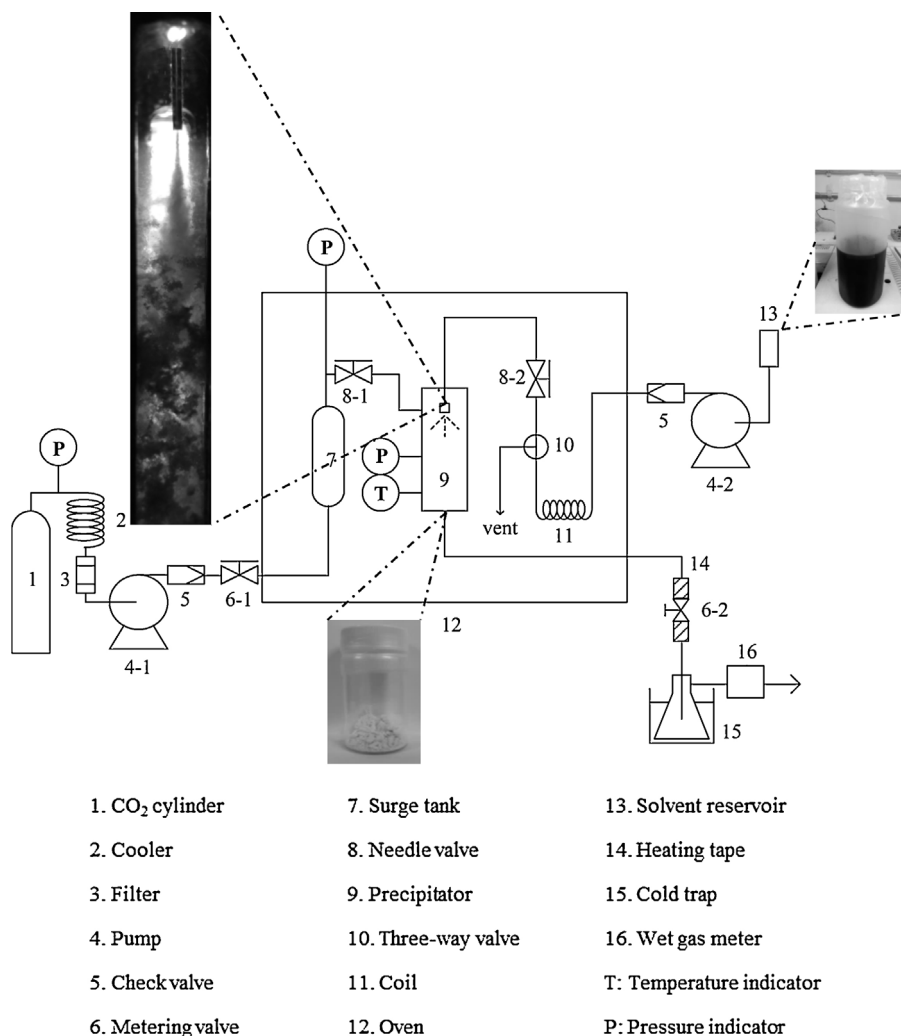


Fig. 1. Experimental apparatus for the precipitation of PAA.

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