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Preparation of Nylon 4 microspheres via heterogeneous polymerization of 2-pyrrolidone in a paraffin oil continuous phase

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ABSTRACT

The successful preparation of Nylon 4 microspheres via heterogeneous polymerization is described. Polymerization of 2-pyrrolidone (C4) was carried out in a paraffin oil/C4 heterogeneous medium containing sodium dodecyl sulfate, potassium tert-butoxide, and benzoyl chloride. The effects of polymerization variables including the stirring speed, phase ratio, and emulsifier and catalyst concentrations on the polymerization were investigated in terms of the polymerization yield, particle size and particle size distribution. By adjusting the experimental conditions, it was possible to prepare coagulation-free Nylon 4 microspheres with a high yield (~76%) with average diameters ranging from 9.6 to 110.9 μm.

Introduction

Q2 The properties of polyamide 4 (Nylon 4) including its tenacity, elongation, elastic recovery, energy to rupture, and moisture regain are similar to or better than those of cotton and other commercially available polyamide fibers [1]. Nylon 4 is easily obtained by anionic polymerization of 2-pyrrolidone, which can be produced from plant matter [2,3]. Nylon 4 is also a biodegradable polymer that decomposes in compost soils and activated sludge [4,5], making it an environmentally promising material with excellent mechanical properties and moisture regain. Although its properties are excellent, it has not yet been commercialized due to its poor thermal stability [6]. Its thermal decomposition occurs rapidly just below its melting point [5,6]. Efforts to improve the thermal stability of Nylon 4 have employed various approaches including chemical modification of chain ends [6,7] or backbone amide groups [8], but only marginal improvements have been reported.

Furthermore, anionic bulk polymerization is a conventional polymerization technique for the synthesis of Nylon 4. As polymerization proceeds up to a certain degree, solidification occurs due to the insolubility of the formed polymer in the monomer, forming a hardened cluster of Nylon 4 [9]. To remove the polymer from a reactor, the cluster is dissolved by adding a solvent such as formic acid and then precipitated out in a non-solvent. However, this process is time consuming and uneconomical.

To overcome the drawbacks of the bulk polymerization process, heterogeneous polymerization of 2-pyrrolidone in paraffin oil has been evaluated. The objectives of this study were to successfully prepare Nylon 4 at a high yield and investigate the effects of experimental variables such as the stirring speed, phase ratio, surfactant concentration and catalyst concentration on heterogeneous polymerization.

Experimental

Materials

2-Pyrrolidone (C4, 99%) monomer, potassium tert-butoxide (t-BuOK, 97%) catalyst, benzoyl chloride (BzC, 99%) initiator, and paraffin oil (puriss) and n-heptane (99%) dispersion mediums were purchased from Sigma–Aldrich. The sodium dodecyl sulfate (SDS, 95%) surfactant was purchased from Wako Pure Chemical Industries. All reagents except for C4, n-heptane and SDS were used as received. Prior to use, C4 and n-heptane were dried over CaH_2 and SDS was purified by recrystallization from ethanol [10].

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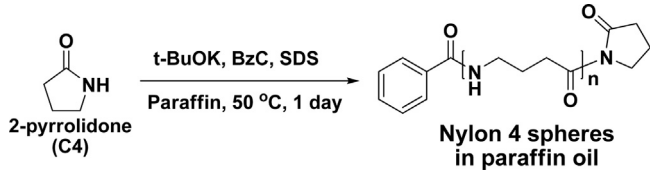

Scheme 1. The heterogeneous polymerization scheme of 2-pyrrolidone.

Characterization

The chemical structure of Nylon 4 was determined by ^{1}H NMR spectroscopy. The spectra were recorded using a Varian-Unity Inova 500NB spectrometer and the polymer samples were dissolved in a 1:1 mixture (v/v) of 2,2,2,-trifluoroethanol (TFE) and chloroform-d ($CDCl_3$). Approximately 0.01 g polymer was dissolved in 0.8 ml TFE/$CDCl_3$ mixture. The intrinsic viscosity ([η]) was measured using a Cannon-Ubbelohde viscometer with a size of 2 in m-cresol at 30 °C.

Differential scanning calorimetry (DSC) thermograms were recorded using a Perkin Elmer DSC 7 at temperatures ranging from 30 to 300 °C at a heating rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) traces were recorded using a Perkin Elmer TGA 7 where 10 mg sample was heated from 25 to 120 °C at a heating rate of 10 °C/min under nitrogen followed by heating for 10 min at 120 °C under nitrogen to ensure dryness. Finally, the sample was heated at a heating rate of 10 °C/min from 120 to 600 °C under nitrogen.

The morphology of the Nylon 4 spheres was observed using a scanning electron microscope (SEM, JSM-7401F, JEOL) where the samples were prepared by diluting a small amount of a Nylon 4 suspension with a large excess amount of n-hexane followed by spreading the diluted mixture on carbon tape, evaporation of the solvents, and, lastly, coating with gold. A laser particle size analyzer (LS-POP (6), OMEC Technology Ltd., Zhuahi, China) was used to measure the average particle size and size distribution. Analyses have been performed on the polymer suspension samples which had been poured in the water circulating chamber of the analyzer and allowed to be stirred for 3 min at room temperature.

Heterogeneous polymerization of 2-pyrrolidone in paraffin oil

All heterogeneous polymerizations were carried out in a 100-ml three-necked flask equipped with a magnetic bar, two stop cocks, a drying tube, and a vacuum apparatus. The vacuum equipment was connected to one stop cock and was used to remove any residual water present in the reaction flask as well as the tert-butanol by-product that formed as a result of the reaction of the monomer and t-BuOK. In order to maintain dryness, a drying tube was attached to the other stop cock.

Table 1
Effect of catalyst concentration on heterogeneous polymerization.[a]

t-BuOK (mol% C4)	Yield (%)[b]	[η] (dL/g)[c]	Average diameter (μm)	Coagulation
10	52	0.9	39.1	Occurred
5	76	0.8	69.6	Did not occur
2.5	46	0.7	26.2	Did not occur

[a] Reaction conditions: C4/BzC = 100/1 mol%, surfactant concentration = 6.25 wt%, C4/dispersion medium = 1/6 (v/v), stirring speed = 500 rpm, reaction time = 1 day, and reaction temperature = 50 °C.
[b] The obtained yield.
[c] Intrinsic viscosity measured in m-cresol at 30 °C.

The typical synthesis of Nylon 4 via heterogeneous polymerization proceeded as follows (Scheme 1). C4 (11.1 g, 0.1304 mol), t-BuOK (0.7317 g, 0.00665 mol), and SDS (0.74 g, 6.25 wt% of monomer) were added to the three neck round bottom flask equipped with a magnetic bar and stirred at 90 °C and a stirring speed of 500 rpm. The dispersion medium, paraffin oil (60 ml), was poured into the reaction flask and stirred under a reduced pressure for 2 h to remove the tert-butanol by-product produced from the reaction of C4 with t-BuOK and any moisture in the paraffin oil. The oil bath was cooled to 50 °C for 1 h and BzC (0.18 g, 0.0013 mol) was added to initiate polymerization. As polymerization proceeded, the transparent mixture changed to an opaque white mixture and then assumed a yellow color. The polymerization reaction was allowed to proceed for 1 day. Finally, the yellowish particles in paraffin were poured into a large excess amount of hexane and stirred for 6 h to completely remove the paraffin oil. The obtained polymer was filtered and washed with acetone/water (9/1, v/v) to remove both SDS and unreacted C4 monomers. The Nylon 4 spheres were dried overnight at 50 °C under vacuum. The results included a yield of 76%, a T_m of 260 °C (by DSC), a [η] value of 0.8 dL/g (Table 1), and a particle average diameter of 69.6 μm. The ^{1}H NMR (TFE/$CDCl_3$) results revealed peaks at 1.74 (quintet, $-CH_2-\underline{CH_2}-CH_2-$), 2.17 (triplet, $-\underline{CH_2}-CO-$), and 3.16 ppm (triplet, $-\underline{CH_2}-NH-$).

To investigate the effect of continuous phase in the heterogeneous polymerization on the particle morphologies, polymerization has also been performed in n-heptane under the same polymerization condition described previously in this section.

Results and discussion

Effect of the dispersion medium on particle morphology

The particle morphology of the Nylon 4 heterogeneous was found to be strongly affected by the nature of the dispersion medium used in the polymerization. Fig. 1 shows SEM photographs of Nylon 4

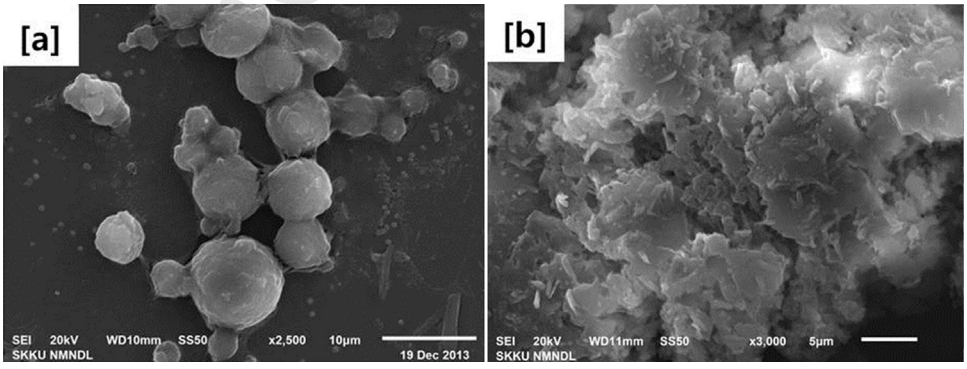

Fig. 1. SEM micrographs of Nylon 4 prepared in (a) t-BuOK (2.5 mol%, Table 1) and (b) n-heptane.

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