Preparation of Nylon-6 Particles in Ionic Liquids

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Summary: Utilizing the thermal stability of ionic liquid, micrometer-sized Nylon-6 particles were successfully prepared by hydrolytic polymerization of ε-caprolactam at high temperature with polyvinyl pyrrolidone as stabilizer in ionic liquids, 1-butyl-3-methyl imidazolium tetrafluoroborate, [Bmim][BF_4] and N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoro-methanesulfonyl)amide, [DEME][TFSA]. The obtained particles had a unique shape because Nylon-6 is a crystalline polymer. Viscosity-average molecular weights of Nylon-6 prepared in [Bmim][BF_4] and [DEME][TFSA] at 180 °C for 48 h were 4200 and 2200, respectively.

Keywords: ε-caprolactam; hydrolytic polymerization; ionic liquid; nylon-6; polymer particle

Introduction

Traditionally and up to the present, large amounts of volatile organic compounds (VOC) have been used as common reaction media for polymer production. However, because the use of VOC has been adverse effects on environment, a shift to environmental friendly media such as water and supercritical carbon dioxide ($scCO_2$)[1–7] is progressing.

In the last decade, the use of ionic liquids arose as an alternative replacement for VOC in electrochemical and separation processes and as media for chemical and biochemical syntheses.[8–11] Ionic liquids, which are salts that melt at ambient temperature, are thought to be environmentally friendly solvents due to their unique properties, such as non-volatility, non-flammability, high chemical and thermal stability. Recently, there has been an increasing amount of research dealing with the application of ionic liquids as solvents for organic synthesis. In the field of polymer chemistry, application of ionic liquids as reaction media for polymerization processes has been receiving much attention.[12–35] We reported the preparation of polystyrene (PS) particles by dispersion polymerization in an ionic liquid.[36] Moreover, successful preparation of PS/poly(acrylic acid) composite particles comprising both hydrophobic and hydrophilic (water soluble) polymers in an ionic liquid has been demonstrated.[37] Utilizing the advantage of the non-volatility of ionic liquids, we also have demonstrated that thermal polymerization of styrene at 130 °C without initiator, relying on thermal initiation of styrene, could be carried out in a conventional reactor (not autoclave). The submicrometer-sized PS particles were successfully prepared.[36]

Nylon-6 is one of the most important polymers as industrial materials for automobile and electronic components. Recently, Nylon-6 particles have been the focus of much attention in fields of industrial materials for biocatalysts and cosmetics because of their functional groups: amine and carboxyl groups. Nylon-6 particles can be prepared by anionic polymerization at relatively low temperature (120∼150 °C). Ricco and co-workers synthesized micrometer-sized Nylon-6 powders by the "fast activated anionic polymerization" of ε-caprolactam in suspension system, in which the continuous phase was composed of polyisobutene oils.[38] Landfester et al. reported the

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preparation of Nylon-6 nanoparticles by anionic polymerization of ε-caprolactam in miniemulsion system in a polar solvent such as dimethyl sulfoxide.[39] Yang et al. prepared Nylon-6 particles via a successively in-situ polymerization method, adjusting phase inversion morphology generated in Nylon-6/polystyrene (PS) blends with very low PS contents.[40] However, anionic polymerization requires strict polymerization conditions and a cumbersome reactor. Nylon-6 has conventionally been prepared by hydrolytic polymerization at high temperature (~250 °C). However, it has been difficult to prepare Nylon-6 particles directly by hydrolytic polymerization in heterogeneous system at high temperature due to the necessity of a suitable solvent.

In this article, utilizing the thermal stability of ionic liquids, Nylon-6 particles were prepared by hydrolytic polymerization of ε-caprolactam at the high temperature in ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME][TFSA]).

Experimental Part

Materials

Reagent grade ε-caprolactam and ε-amino-n-caproic acid were used as received. Water used in all experiments was obtained from Elix® UV (Millipore Co., Ltd.; Japan) purification system and had a resistivity of 18.2 μΩ · cm. Poly(vinyl pyrrolidone) (PVP, K-30, weight-average molecular weight 3.6×10^5 g/mol) as a stabilizer was used as received. Reagent grade [Bmim][BF_4] was used as received. [DEME][TFSA], provided by Nisshinbo Industries Inc., Tokyo, Japan, was used as received.

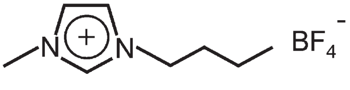
Preparation of Nylon-6 Particles by Hydrolytic Polymerization in Ionic Liquids

Hydrolytic polymerizations of ε-caprolactam (0.78 g) in [Bmim][BF_4] or [DEME][TFSA] (2.5 g) with a catalyst were carried out in sealed glass tubes under a nitrogen atmosphere at 180, 200 and 250 °C in an oil bath for 24, 48 and 96 h. Water (0.04 g) or ε-amino-*n*-caproic acid (0.22 g) was added as catalyst for ring opening of ε-caprolactam and PVP was used as colloidal stabilizer. The sealed glass tubes were shaken horizontally at 80 cycles/min (3-cm strokes).

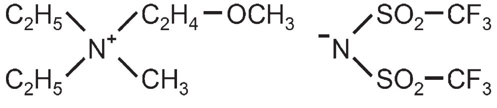
Characterization

Nylon-6 particles were observed by scanning electron microscopy (SEM, S-2460, Hitachi Science Systems Ltd., Ibaraki, Japan) after centrifugal washings with methanol and water (two and three times), which is miscible with [DEME][TFSA] and [Bmim][BF_4]. The conversions were measured by gravimetry. The intrinsic viscosity ($[\eta]$) was measured by an Ubbelohde viscometer with *m*-cresol as the solvent at 25 °C. The viscosity average molecular weight (M_v) was calculated from the intrinsic viscosity using the Mark-Houwink-Sakurada equation: $[\eta] = 1.8 \times 10^{-3} M_v^{0.654}$.[41]

Thermal gravimetric analyses of the ionic liquids were carried out with Seiko Instrument TG/DTA 220U at the heating rate of 10 °C/min up to 500 °C in N_2 atmosphere. The thermal stability of the ionic liquids was confirmed by monitoring the weight loss from 30 to 500 °C by TG-DTA. No weight loss was detected at temperatures below 350 °C, confirming that both ionic liquids ([DEME][TFSA] and [Bmim][BF_4]) are suitable for high temperature polymerizations.



[Bmim][BF_4]



[DEME][TFSA]

Results and Discussion

In conventional dispersed systems, a suitable colloidal stabilizer has affinity for both a medium and polymer particles. PVP is commonly used as stabilizer in dispersion polymerizations in organic solvents.[42–46] Since PVP is soluble in [Bmim][BF_4] and [DEME][TFSA], PVP was chosen as stabilizer in this experiment. In order to dissolve water required for the ring-opening reaction of ε-caprolactam, the hydrophilic ionic liquid, [Bmim][BF_4], which is compatible with water, was used as medium first. Before polymerization, the system was homogeneous, that is, ε-caprolactam, water and PVP are soluble in [Bmim][BF_4]. After 24 h, though the system was discolored, it was homogeneous indicating that no Nylon-6 particle was formed.

Reaction scheme for the synthesis of Nylon-6 by hydrolytic polymerization is shown in Figure 1. Hydrolytic polymerization of ε-caprolactam involves three principle reactions: (1) ring opening: the ε-caprolactam is hydrolyzed to give ε-amino-*n*-caproic acid, which acts as initiator. (2) polycondensation: condensation takes place between the amino and carboxyl groups of two different ε-amino-*n*-caproic acid molecules and oligomers. (3) polyaddition: the amino groups of ε-amino-*n*-caproic acid and oligomer chain are the stronger nucleophile and can open the ring of ε-caprolactam. In order to obtain Nylon-6 of high molecular weight, it is necessary to remove by-products, water, because polycondensation is an equilibrium reaction. In an above case, it was considered that the initially added water obstructed the polymerization and the equilibrium should be achieved at the early stage of the polymerization because the polymerization was carried out in the closed system to prevent from oxidation of ε-caprolactam.

To depress the influence of water, ε-amino-*n*-caproic acid was used instead of water, which is also able to act as ring opening catalyst.[47] Moreover, in addition to the [Bmim][BF_4] system, hydrophobic ionic liquid, [DEME][TFSA] was used as medium in order to eliminate water from polymerization system during polymerization. After polymerization, both polymerization mixtures were also homogeneous, but became turbid during the cooling process, which indicates the formation of PS particles. The obtained particles observed with SEM (Figure 2a, d) were micrometer-size and had unique shape

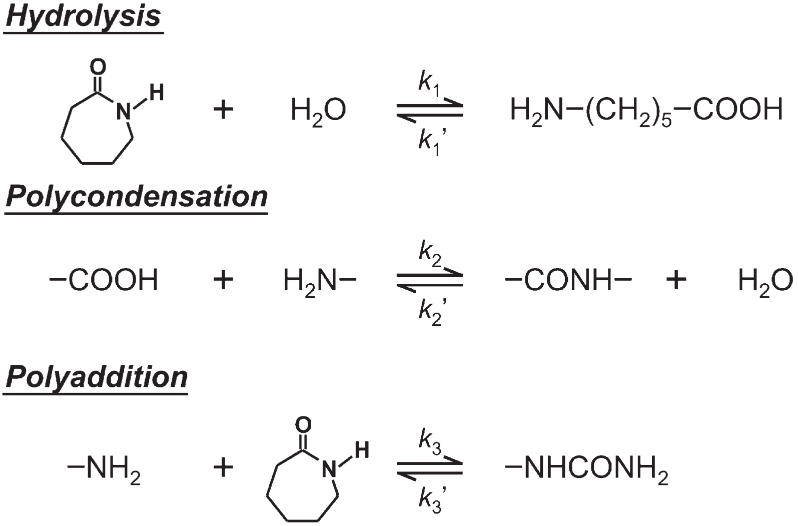


Figure 1.
A synthesis of Nylon-6 by hydrolytic polymerization.

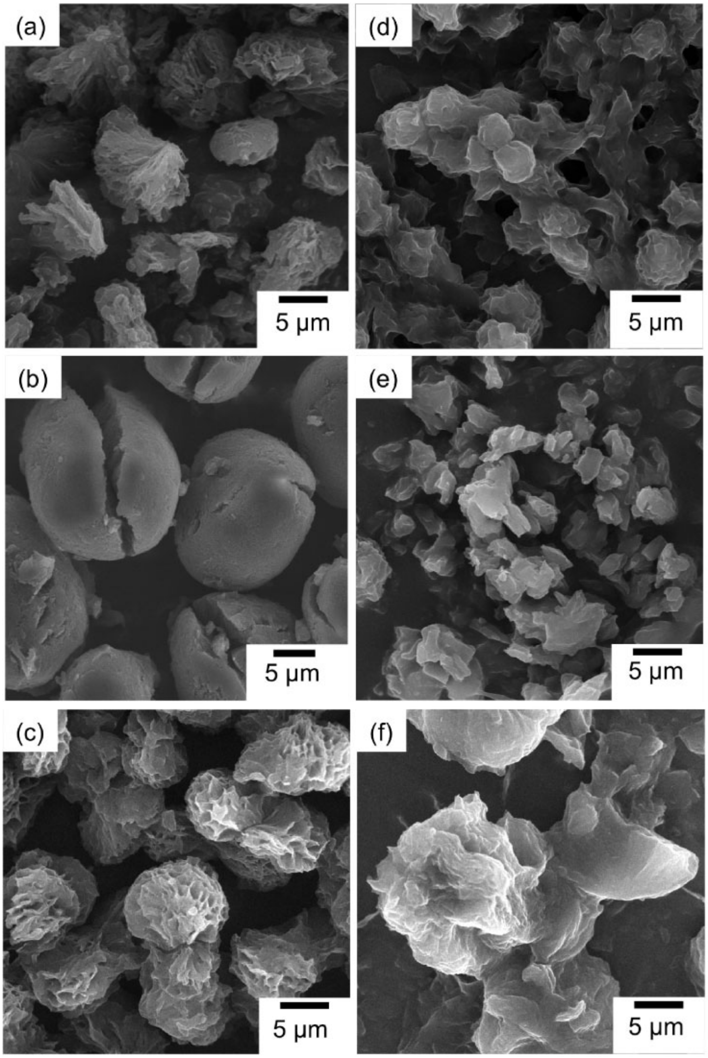


Figure 2.
SEM photographs of Nylon-6 particles prepared by hydrolytic polymerizations at 180 °C for 24 h (a, d), 48 h (b, e) and 96 h (c, f) in different ionic liquids: (a, b, c) [Bmim][BF_4]; (d, e, f) [DEME][TFSA].

because Nylon-6 is a crystalline polymer. In the case of PVP-absence system, the system was colloidally unstable and coagulum was obtained.

M_v value of Nylon-6 prepared in [Bmim][BF_4] and [DEME][TFSA], calculated from the intrinsic viscosities using Mark-Houwink-Sakurada equation, were 700 and 1200, and degree of polymerization were 6 and 10, respectively.

To obtain high molecular weight Nylon-6, the polymerization time was extended from 24 to 48 h in both systems. As for 48 h, the systems were turbid at 180 °C during the polymerizations without cooling to room temperature, indicating that the polymerizations proceeded well. Obtained particles are shown in Figure 2b, e. The particle shape became somewhat spherical, which may be caused by the increase in degree of polymerization of Nylon-6. M_v values of Nylon-6 prepared in [Bmim][BF_4] and [DEME][TFSA] for 48 h increased to 4200 and 2200, respectively. On the other hand, as for 96 h systems (Fig. 2c, f), M_v values decrease to 1800 and 620, respectively. It was likely that depolymerization or cyclization reaction would preferentially proceed in comparison to propagation reaction during the long reaction time. Moreover, the propagation reaction of polycondensation, which is intra-molecular reaction, is should be reduced in solution and dispersion polymerization systems, in which monomer concentrations were low. In general, a hydrolytic polymerization was carried out in a bulk system.

Figure 3 shows the effect of monomer concentration on conversion and M_v for hydrolytic polymerization of ε-caprolactam in [Bmim][BF_4] at 180 °C for 48 h. Both the conversion and M_v increased with increasing monomer concentration, which is consistent with above explanation.

A hydrolytic polymerization of ε-caprolactam is also generally carried out in the temperatures range from 220 to 270 °C in the presence of appropriate amounts of water or water releasing materials, such as ε-amino-*n*-caproic acid, under the oxygen-free conditions. However, in this experiment, M_v values of Nylon-6 prepared at 200 and 250 °C were very low. This might be because high polymerization temperature causes significant reverse reactions (hydrolysis) in ionic liquids,[48] or side reactions such as thermal and oxidative decompositions, and a cyclization in the case of low monomer concentration.

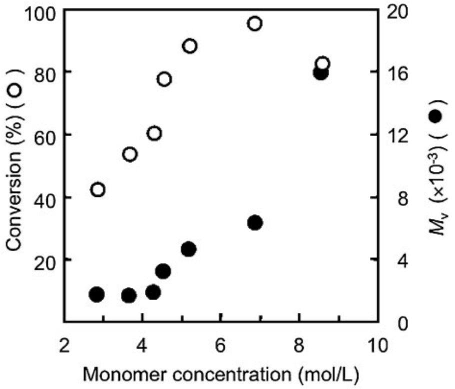


Figure 3.
Conversion (○) and M_v (●) vs. monomer concentration plots for hydrolytic polymerization of ε-caprolactam at 180 °C for 48 h in [Bmim][BF_4].

Conclusions

Micrometer-sized, Nylon-6 particles were successfully prepared by hydrolytic polymerization of ε-caprolactam in [Bmim][BF_4] and [DEME][TFSA] with ε-amino-*n*-caproic acid as catalyst at 180 °C. The highest M_v was obtained when hydrolytic polymerization of ε-caprolactam was conducted in [Bmim][BF_4] at 180 °C for 48 h. This study suggests that the choice of ionic liquids and a polymerization condition such as polymerization time is important to increase M_v. The results obtained in this experiment also indicate that ionic liquids have great advantage as the medium for preparation of functional polymer particles require high temperature.

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