Colloid Polym Sci (2007) 285:535–541
DOI 10.1007/s00396-006-1601-9

ORIGINAL CONTRIBUTION

Preparation of micron-sized aromatic polyamide particles using ultrasonic irradiation

Yayoi Yoshioka · Katsuya Asao · Kazuhiko Yamamoto · Hideki Tachi

Received: 21 April 2006 / Accepted: 18 September 2006 / Published online: 21 November 2006

Abstract Aromatic polyamide particles were prepared by reacting *p*-phthalyl chloride and 4,4′-diaminodiphenyl ether in an acetone solution with a high water content, using a precipitation polymerization method with ultrasonic irradiation. The average particle diameter was ca. 712 nm, and the particles were porous and spherical with a narrow size distribution. They showed a high degree of crystallinity and excellent thermal stability. The morphology and the thermal decomposition temperature of the submicron particles were found to depend strongly on the volume of water added to the reaction system. In this polymerization method, the addition of water was essential for the formation of spherical particles. The simultaneous mixing process resulted in the formation of particles with a narrow size distribution, and the use of ultrasonic irradiation was effective in reducing particle size.

Keywords Submicron particles · Aromatic polyamides · Ultrasonic irradiation

Introduction

Aromatic polyamides have rigid chemical structures consisting mainly of benzene rings and amide groups. They have excellent chemical resistance and mechanical and thermal properties [1–6]. Polyamide is insoluble in conventional solvents, but soluble in strong acids such as sulfuric and hydrochloric acid [4]. Due to its excellent mechanical properties, it cannot be broken into fine particles, and it needs much thermal energy to reach the molten state. These characteristics make it difficult to mold polyamide materials in secondary processes, and consequently, aromatic polyamides are limited to uses such as fiber and bulk. A well-known use for these compounds is in aramid fibers [5], which are used for flak jackets and reinforcing materials.

The preparation of aromatic polyamide microcapsules has recently been reported [7]. However, there have been no reports of micron-sized aromatic polyamide particles with a narrow particle size distribution. Recently, polymer particles with a narrow particle size distribution, which have possible application as spacers for display purposes, medical carriers, and chromatographic carriers, have been the subject of much attention [8–14]. There were many reports concerning the preparation methods and applications of polymethyl methacrylate and polystyrene particles [12–20]. The mechanical, thermal, and chemical resistance properties of these particles, however, are inferior to those of aromatic polyamide particles; aromatic polyamide particles are likely to be used in high value-added products.

Suspension and emulsion polymerization are conventional methods of preparing polymer particles [18–23]. To induce particle formation and prevent aggregation, these methods require the use of a certain quantity of stabilizer or surfactant, which eventually remains on the particle surface due to either physical adsorption or chemical bonding. This sometimes affects the properties of particles or composited materials. For preparation methods without the use of stabilizers or surfactants, the phase separation phenomenon is utilized. Micron-sized aliphatic polyamide particles (i.e., nylon particles) with a narrow particle size distribution

---

Y. Yoshioka (✉) · K. Asao · K. Yamamoto · H. Tachi
Department of Environment and Chemistry,
Technology Research Institute of Osaka Prefecture,
2-7-1, Ayumino, Izumi,
Osaka 594-1157, Japan
e-mail: yoshioka@tri.pref.osaka.jp

were reported to be useful for this purpose and are used commercially by some companies [8, 23–29]. In some cases [25–29], the dissolved polyamides are induced to undergo phase separation by lowering the solution temperature or by gradually adding solvent. In these methods, product formation takes a long time, and accurate control of temperature or solubility is required for production of uniform polymer particles.

Recently, we discovered a new and simple preparation method for fabrication of micron-sized aromatic polyamide particles [30]. The aromatic polyamide particles were prepared using a precipitation polymerization method, with the use of ultrasonic irradiation. A diamine and a diacid chloride underwent a condensation reaction in an acetone solution containing water. Generally, water is forbidden in condensation reactions, but in this reaction system, a considerable volume of water was added. Furthermore, although micron-sized aliphatic polyamide particles were previously reported, micron-sized aromatic polyamide particles have not yet been reported. Investigation of this reaction mechanism will provide important information on the formation of particles and on condensation reactions of polyamide. This paper introduces the polymerization method and discusses the characteristic features of the resulting aromatic polyamide particles.

Experimental

Materials

P-phthalyl chloride was purchased from Tokyo Kasei, Japan, and 4,4′-diaminodiphenyl ether was purchased from Wakayama Seika, Japan. Acetone, which was purchased from Kishida Chemical, Japan, was used as the polymerization reaction solvent. These compounds and solvents were used as received, without any further purification.

Particle preparation

P-phthalyl chloride (0.0005 mol) and 4,4′-diaminodiphenyl ether (0.0005 mol) were each dissolved in 50 ml acetone. Distilled water was added in varying amounts (e.g., 25 ml) to the 50 ml 4,4′-diaminodiphenyl ether solution, followed by addition of the entire *p*-phthalyl chloride solution at once. The solution was subjected to ultrasonic irradiation at 45 kHz in a water and ice bath during mixing and for a period of 20 min thereafter. The product was extracted using centrifugal separation and washed with acetone and water to dissolve any unreacted monomer. This process was carried out five times to achieve full purification. The sample was then dried overnight in a vacuum oven at 100 °C.

Characterization

The particles obtained were sputtered with a gold coating, and their morphology was investigated using a Hitachi Fe-SEM S-4700 scanning electron microscope (SEM; Hitachi, Japan). Particle size distribution was measured in a water dispersion using a Photal ELS-8000 Laser Zeta potential analyzer (Otsuka Electronics, Japan). The specific area of the particles was measured using a Yuasa Autosorb-1 surface area and pore size analyzer (Yuasa, Japan). The X-ray diffraction profiles of the samples were measured using a Rigaku RINT-2500 X-ray diffractometer (Rigaku, Japan) with graphite monochromatized Cu–Kα radiation and a scan speed of 1°/min. The IR spectra of the samples were measured using a PerkinElmer Spectrum One infrared spectrometer (PerkinElmer, USA) in KBr tablets at a resolution power of 4 cm^{-1}. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Seiko TG/DTA 320 U analyzer (Seiko, Japan) by heating the samples in a nitrogen atmosphere at a rate of 10 °C/min.

Results and discussion

Effect of volume of water added

Morphology

The influence of the volume of water added to this reaction system on the morphology of the resulting aromatic polyamide was investigated. The volume of water added was varied in steps of 5 ml over a range of 0–50 ml for 100 ml of acetone solution (i.e., 50 ml *p*-phthalyl chloride solution and 50 ml 4,4′-diaminodiphenyl ether solution). SEM photographs of some of the products are shown in Fig. 1a–g. The product prepared without water was in bulk rather than particulate form (Fig. 1a). The average particle diameter decreased as the volume of water added increased. The morphology was found to depend on the volume of water added. Based on the SEM photographs, we judged that, in order to obtain spherical particles, the most suitable amount of water for this reaction system was 25 ml (Fig. 1d). The addition of water was found to be essential for the formation of spherical particles, and the formation of particles was strongly associated with the polarity of the reaction solution. Accordingly, water is thought to play an important role as an adjuster of the polarity of the reaction solution in this polymerization system.

Polymerization and hydrolysis

It is curious that a diamine and a diacid chloride underwent condensation in a reaction solvent with a high water

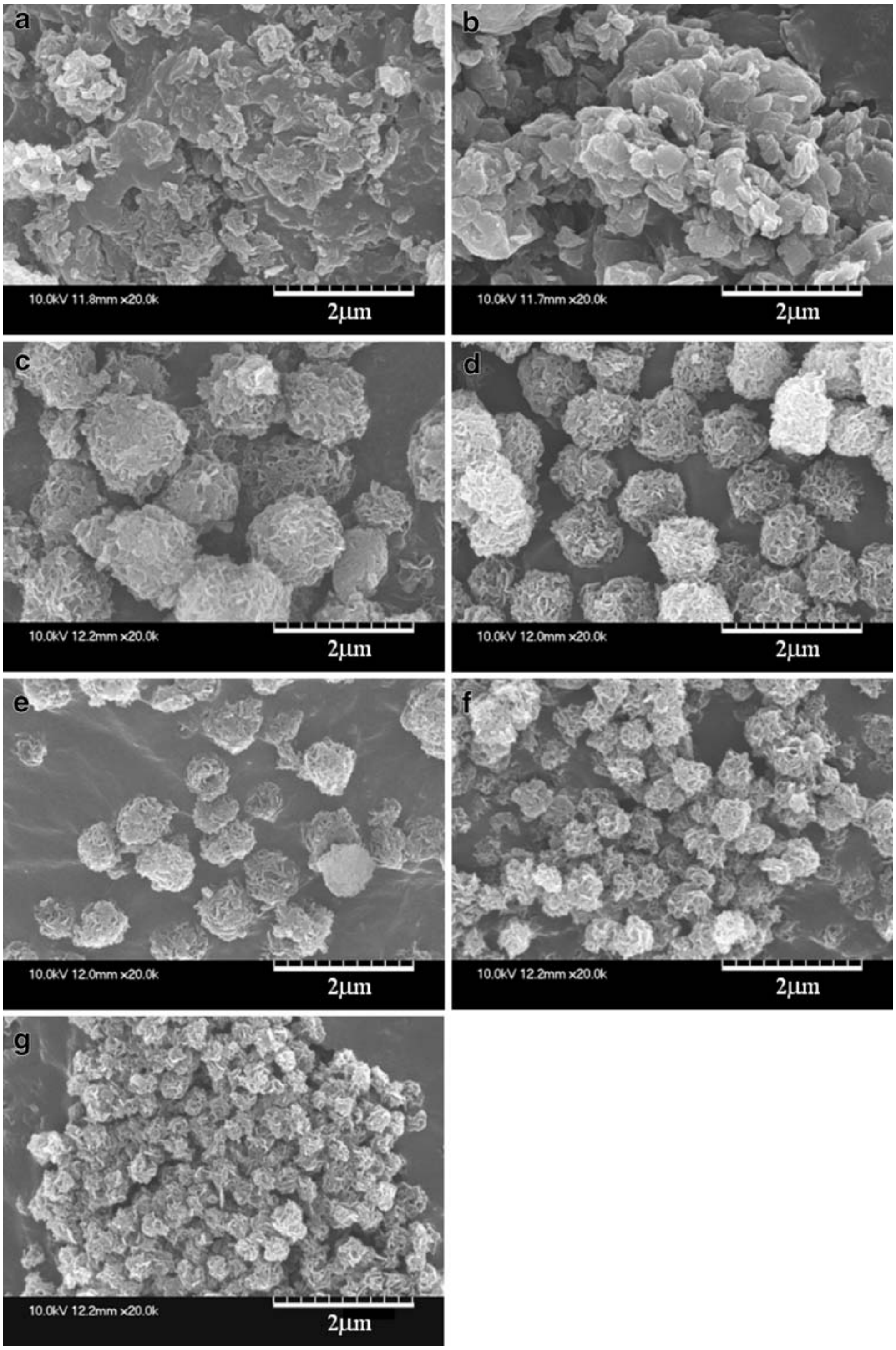

Fig. 1 SEM photographs of polyamide products. Volume of water added to reaction system (100 ml acetone solution): **a** 0, **b** 10, **c** 20, **d** 25, **e** 30, **f** 40, and **g** 50 ml

content. In general, the use of water should be avoided in condensation reactions; in this case, water should convert the acid chloride to a carboxylic acid (hydrolysis reaction), inhibiting the reaction between amine and acid chloride. The possibility of hydrolysis reactions in this polymerization system was considered. As mentioned in the "Experimental" section, the diacid chloride solution was poured all at once into the diamine and water solution, allowing the diacid chloride to react with both the diamine and the water. However, practically, the diacid chloride seems to react preferentially with the diamine rather than the water. An evidence for this was the fact that the conversion rates of all polyamide products obtained were above 94%. In the infrared spectra of the products, characteristic bands due to aromatic polyamide bonds were observed: for example, 3,297 cm^{-1} [amide A (N–H stretching mode)], 1,646 cm^{-1} [amide I (C=O stretching mode)], and 1,534 cm^{-1} [amide II (coupling of C–N stretching and N–H in-plane bending modes)]. The thermal decomposition temperatures (T_d) of the products were estimated by TG/DTA measurement. Figure 2 shows a plot of T_d at 5 wt% weight loss against the volume of water added. All T_d values obtained were above 395 °C, indicating that the products were not monomers or low molecular weight polyamides, such as oligomers, but high molecular weight polyamides.

Thermal properties such as T_d generally depend on molecular weight. Investigation of the behavior of T_d should provide significant information about molecular weight and degree of polymerization for polymers that are insoluble in conventional solvents. As shown in Fig. 2, T_d increased rapidly as the amount of water added increased from 0 to 25 ml and was almost constant from 25 to 50 ml. The behavior of T_d in the range 0–25 ml indicates that the molecular weight of the resulting polymer increases with the volume of water added. It can be speculated that the addition of water accelerates the polymerization reaction of the diamine and the diacid chloride. Generally, a reaction accelerator such as pyridine is added to condensation polymerization reactions of diamine and diacid chloride to remove HCl generated during the reaction, because HCl disturbs the polymerization reaction, resulting in a lower molecular weight product. In the above-described reaction system, water is thought to play this role. Figure 3 shows the infrared spectra of these products obtained in the region of 1,800–4,000 cm^{-1}. There were two strong bands at ca. 2,850 and 2,590 cm^{-1} in the spectrum of the product prepared without water, corresponding to the hydrochloride salt of an amine (–NH_3Cl) [31]. The appearance of these two bands indicates that the polyamide obtained is complexed with HCl, strictly speaking, that the amine end groups of the polyamide are capped with HCl. As shown in Fig. 3, these two bands decreased markedly in intensity as the volume of water added increased. Therefore, it was concluded that water removed HCl out of this reaction system. Additional detailed information will be provided in the near feature. In the region of 25–50 ml, it can be speculated that the polyamide products have relatively high molecular weights above a certain level, although a concrete value cannot be obtained. Based on these results and the conversion values obtained, it appears that condensation polymerization takes place in preference to hydrolysis in this reaction system.

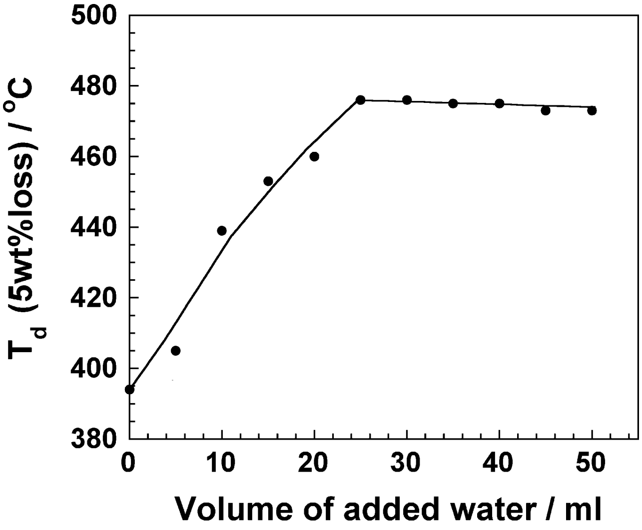

Fig. 2 Plot of T_d (thermal decomposition temperature at 5 wt% loss) against volume of water added

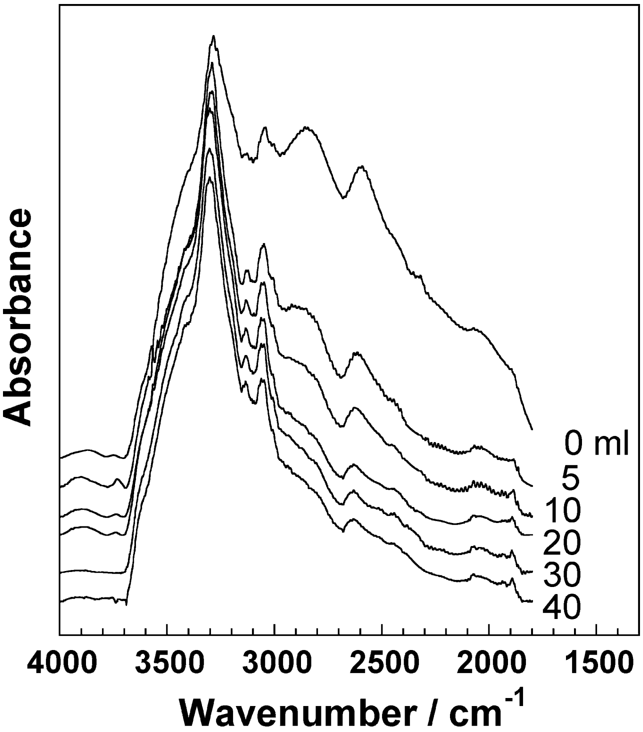

Fig. 3 Infrared spectra of polyamide products in the region of 1,800–4,000 cm^{-1}. Volume of water added to reaction system (100 ml acetone solution), from *top* to *bottom*: 0, 5, 10, 20, 30 and 40 ml

Characteristics of aromatic polyamide particles

As shown in Fig. 1d, the aromatic polyamide particles obtained were porous spherical particles with a narrow size distribution. Figure 4 is a magnified version of Fig. 1d. Figure 5 shows the particle size histogram estimated by particle size distribution measurement. The average particle diameter and standard deviation were estimated to be 712 and 81 nm, respectively; the corresponding values estimated from SEM images of 100 particles selected at random were 750 and 69 nm, respectively, which were in close

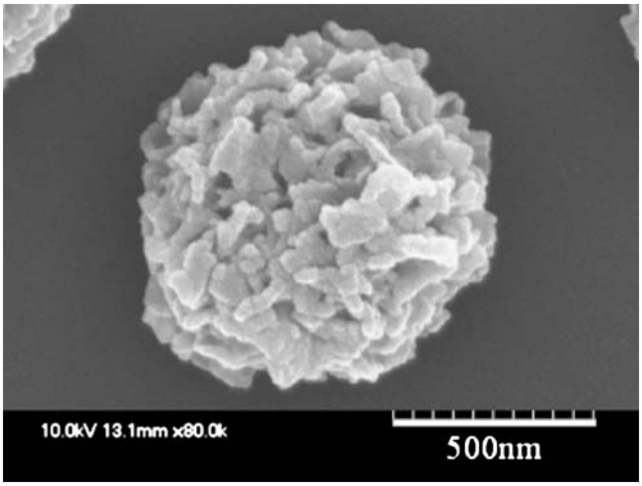

Fig. 4 SEM photographs of aromatic polyamide particles at 80,000-fold magnification

agreement. The specific surface area was estimated, using the nitrogen gas adsorption method, to be 106.7 m^2/g. This value is much higher than that calculated for spherical particles with smooth surfaces (the theoretical figure for a particle 712 nm in diameter is 5.0 m^2/g), which can be attributed to the porous spherical morphology of the particles as seen in the SEM photograph. Figure 6 shows the X-ray diffraction pattern of these particles. Some sharp peaks were detected, indicating a high degree of crystallinity. The thermal decomposition temperature (T_d) at 5 wt% loss, estimated from TG/DTA measurement, was 477 °C without melting, which indicates excellent thermal stability. Due to their characteristics of thermal stability and large specific surface area, these particles may be applied as efficient chromatographic, catalytic, and medical carriers.

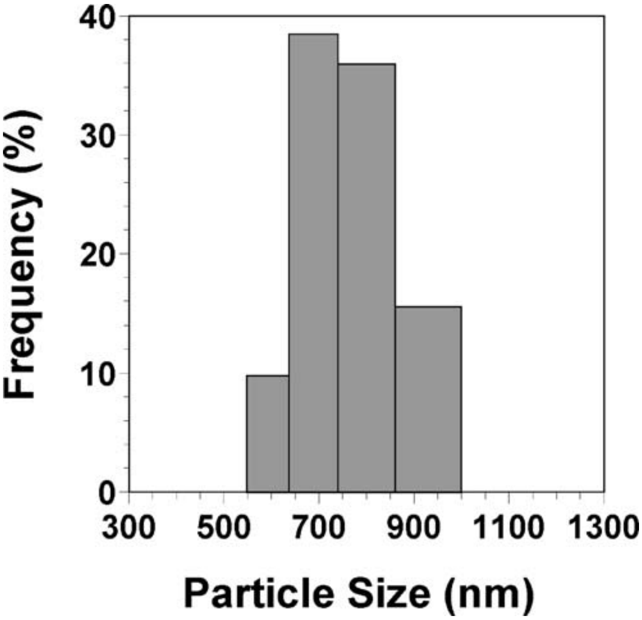

Fig. 5 Particle size distribution histogram

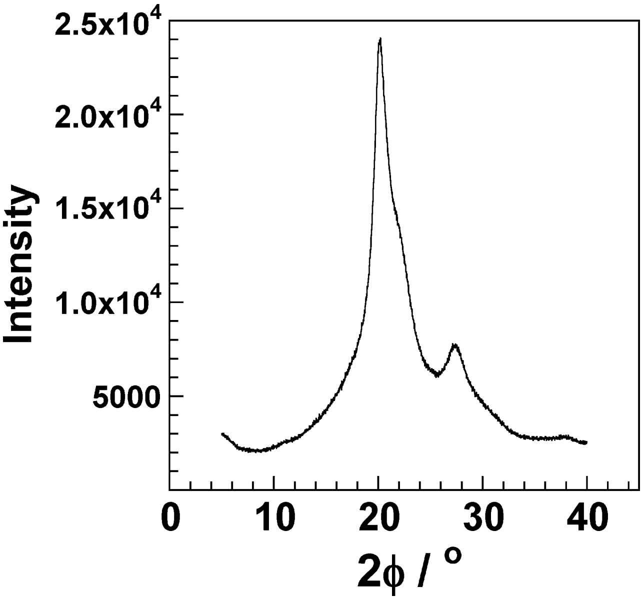

Fig. 6 X-ray diffraction pattern of polyamide particles

Mechanism of particle formation

To clarify the influence of mixing and stirring in the reaction system, we conducted a controlled experiment by performing the polymerization in four different ways (experiments I–IV), and compared the morphologies of the resulting polyamide particles. The experiments were performed under identical conditions, except for the choice of mixing/stirring and the manner of addition of the diacid chloride. In experiment I, the preparation method proposed in this paper was used; that is, the diacid chloride solution was poured all at once into the diamine solution containing 25 ml water, and the mixture was subjected to ultrasonic irradiation for a period of 20 min. In experiment II, the diacid chloride solution was poured all at once into the diamine solution containing 25 ml water, and the mixture was stirred with a magnetic stirrer for a period of 20 min. In experiment III, the diacid chloride solution was delivered dropwise into the diamine solution containing 25 ml water at a continuous speed of 2.5 ml/min under ultrasonic irradiation, and the mixture was then sonicated for a period of 20 min. In experiment IV, the diacid chloride solution was delivered dropwise at a continuous speed of 2.5 ml/min with magnetic stirring, which was continued after addition for a period of 20 min. Figure 7a–d shows SEM photographs of the polyamide products obtained in experiments I–IV, respectively. In experiment I (Fig. 7a), the polyamide particles obtained had an average diameter of ca. 712 nm and showed a narrow size distribution, as mentioned in the previous chapter. In experiment II (Fig. 7b), spherical particles with a relatively narrow size distribution were obtained. The average diameter of the polyamide particles was ca. 1.5 μm (1,500 nm), which was

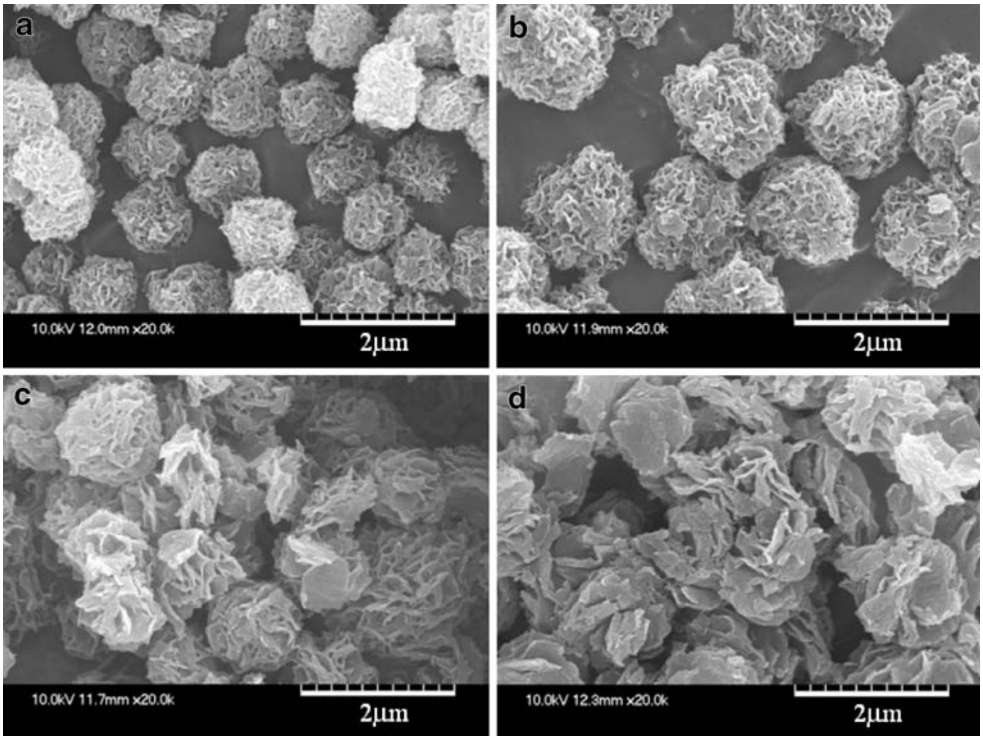

Fig. 7 SEM photographs of polyamide products obtained in experiments I (**a**), II (**b**), III (**c**), and IV (**d**)

larger than that of the particles obtained in experiment I. In experiment II, the magnetic stirring rate did not have a significant influence on the average diameter of the resulting polyamide particles. The particles shown in Fig. 7c (experiment III) are roughly spherical, but an exact form is lacking. For experiment IV (Fig. 7d), the particles obtained were formless. Comparing Fig. 7a,b with Fig. 7c, d, it can be seen that the mixing method in which the diacid chloride solution is poured all at once into the diamine and water solution results in the formation of particles with a narrow size distribution. This indicates that the simultaneous mixing process may result in the concurrent generation of small particle nuclei. The growth mechanism of particles, as shown in Fig. 7a,b can be speculated to be as follows: when the reaction solutions are quickly mixed, small particle nuclei are formed, which grow individually at the same reaction rate. Above a certain particle size, the particles are precipitated, so that particles with a narrow size distribution are obtained. On the other hand, the falling-drop mixing process results in the time lag among the generations of small particle nuclei. The particle nuclei grow individually at different reaction rates because their growth stages are different. Consequently, the particles obtained show a broad size distribution or some aggregation, as shown in Fig. 7c, d. From these results, it was concluded that the simultaneous mixing is the effective process for preparing particles with a narrow size distribution.

Comparing Fig. 7c,d, it can be seen that the particles shown in Fig. 7c are more spherical than those in Fig. 7d. In addition, the particles shown in Fig. 7a are more spherical than those in Fig. 7b, although the difference is not as remarkable. From these results, it was concluded that stirring plus ultrasonic irradiation is the most effective method for forming spherical particles. Furthermore, the average diameter of the particles shown in Fig. 7a is much smaller than that of the particles in Fig. 7b, indicating that ultrasonic irradiation was effective in reducing particle size. This preparation method employing ultrasonic irradiation may be applicable to the fabrication of other types of polymer particles.

Conclusions

Aromatic polyamide particles were prepared by reacting *p*-phthalyl chloride and 4,4′-diaminodiphenyl ether in an acetone solution containing water, using a precipitation polymerization method that employs ultrasonic irradiation. The particles obtained were porous and spherical, with a narrow size distribution. The average particle diameter was ca. 712 nm, and the particles showed a high degree of crystallinity and excellent thermal stability. The morphology and the thermal decomposition temperature T_d of the submicron particles were found to depend strongly on the volume of water added to the reaction system. In this polymerization method, the addition of water is essential for the formation of spherical particles. Water is thought to play two important roles: adjusting the polarity of the reaction solution and acting as a reaction accelerator. The simultaneous mixing process resulted in the formation of particles with a narrow size distribution, and the use of ultrasonic irradiation resulted in a reduction in size. These particles, which have a large specific surface area and excellent thermal stability, may be applied as efficient chromatographic, catalytic, and medical carriers.

Acknowledgements This work was supported by a Grant-in-Aid for Scientific Research of the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References

1. Morgen PW (1977) Macromolecules 10:1381
2. Kwolek SL, Morgen PW, Schaefgen JR, Gulrich LW (1977) Macromolecules 10:1390
3. Bair TI, Morgen PW, Killian FL (1977) Macromolecules 10:1396
4. Arpin M, Strazielle C (1977) Polymer 18:591
5. Yang HH (1993) Kevlar aramid fiber. Wiley, Chichester, UK
6. Li XG, Huang MR (1999) J Appl Polym Sci 71:565
7. Laguecir A, Louhaichi MR, Burgard M (2004) Current Drug Delivery 1:111
8. Mohy Eldin MS, Shoroen CGPH, Janssen AEM, Mita DG, Tramper J (2000) J Mol Catal B Enzym 10:445
9. Ni H, Kawaguchi H (2004) J Polym Sci 42:2833
10. Lin C, Zang Z, Zheng J, Liu M, Zhu XX (2004) Macromol Rapid Commun 25:1719
11. Vennes M, Zentel R (2004) Macromol Chem Phys 205:2303
12. Duguet E, Abbound M, Morvan F, Maheu P, Fontanille M (2000) Macromol Symp 151:365
13. Huang X, Brittain WJ (2001) Macromolecules 34:3255
14. Imbert-Laurenceau E, Berger MC, Pavon-Djavid G, Jouan A, Migonney V (2005) Polymer 46:1277
15. Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW (1986) J Polym Sci Polym Chem Ed 24:2995
16. Okubo M, Fujibayashi T, Terada A (2005) Colloid Polym Sci 283:793
17. Guo W, Durant YG, Wang J, Wu C (2005) J Appl Polym Sci 96:829
18. Shim SE, Cha YJ, Byun JM, Choe S (1999) J Appl Polym Sci 71:2259
19. Kemmere MF, Mayer MJJ, Meuldijk J, Drinkenburg AAH (1999) J Appl Polym Sci 71:2419
20. Yuem JH, Deng Y (2005) Colloid Polym Sci 283:1172
21. Lovell PA, El-Aasser MS (1997) Emulsion polymerization and emulsion polymers. Wiley, New York
22. Boguslavsky L, Baruch S, Margel SJ (2005) J Colloid Interface Sci 289:71
23. Crespy D, Landfester K (2005) Macromolecules 38:6882
24. Karasinski FJ, Ferraro CF (1971) J Colloid Interface Sci 36:195
25. Hou WH, Lloyd TB (1992) J Appl Polym Sci 45:1783
26. Hou WH, Lobuglio TM (1994) J Appl Polym Sci 54:1363
27. Kohan MI (1995) Nylon plastics handbook. Hanser/Gradner Publications, Cincinnati, OH, USA
28. Park Y, Curtis CW, Roberts CB (2002) Ind Eng Chem Res 41:1504
29. Asano Y, Nakayama K, Yao S (2003) J Appl Polym Sci 90:2432
30. Yoshioka Y, Asao K, Yamamoto K, Tachi H (2004) Polym Prepr Jp 53:1182
31. Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG (1991) The handbook of infrared and raman characteristic frequencies of organic molecules. Academic, California, USA