Colloid Polym Sci (2008) 286:1157–1164
DOI 10.1007/s00396-008-1877-z

ORIGINAL CONTRIBUTION

Preparation of nano-sized polybenzimidazole and carbon particles via poly(amino-amide) particles

Yayoi Yoshioka · Katsuya Asao

Received: 29 February 2008 / Revised: 16 April 2008 / Accepted: 19 April 2008 / Published online: 16 May 2008

Abstract Poly(amino-amide; PAA) particles consisting of *p*-phthalyl chloride and 3,3′-diaminobenzidine and 4,4′-diphenyldicarbony chloride and 3,3′-diaminobenzidine were prepared. The particles were then transformed by treatment with heat into poly(*p*-phenylenebenzimidazole; PPC–PAA) and poly(4,4′-diphenylenebenzimidazole; DPC–PAA) particles, respectively. The number ratio of ring-closing of the obtained product was found to be dependent on the processing temperature. However, the morphology and diameter of the products were not found to be temperature dependent. PPC–PAA particles were amorphous and DPC–PAA particles had a high degree of crystallinity. Further, upon heating up to 1,000 °C, poly(*p*-phenylenebenzimidazole) and poly(4,4′-diphenylenebenzimidazole) particles were transformed into carbon particles and carbon bulk, respectively. The poly(amino-amide), polybenzimidazole and carbon particles obtained were nano-sized spherical particles with narrow size distributions.

Keywords Nanoparticles · Poly(amino-amide) · Polybenzimidazole · Carbon · Heat treatment

Introduction

Submicron and nano-sized particles with narrow size distributions have been actively investigated, and a number of particles have been practically utilized. Recently, particles have received much attention not only for their unique morphological properties, but also for their characteristic features and functions to satisfy practical applications in a number of different fields. Thus, particles with unique properties are expected to be useful for high value-added products.

For example, electronic properties are highly desirable for a number of applications. Polybenzimidazole is known to have excellent insulating properties as well as show excellent optical and thermal properties. Thus, there have been several reports on the synthesis and characterization of polybenzimidazoles [1–14]. Melt condensation polymerizations have been reported in which aromatic tetramines and aromatic dicarboxylic acids were heated up to 250–300 °C under nitrogen [1, 2]. The obtained product was then powdered and reheated to 400 °C under high vacuum. Thus, this method requires high reaction temperatures during the two steps. On the other hand, polybenzimidazole was prepared at 200 °C with polyphosphoric acid as the condensing agent for solution based polymerizations [3, 5, 8]. *N*,*N*-dimethylacetamide (DMAc) or tetramethylene sulfone was used as the reaction solvent. However, this method requires troublesome purification procedures such as neutralization of polyphosphoric acid and complete elimination of the reaction solvent, which has a high boiling point. The residual condensation agent and solvent have a considerable influence on the characteristic features and stability of the product. Therefore, these methods are unattractive as commercial polymerization processes.

It is difficult to mold polybenzimidazole materials in secondary processes because of its excellent chemical resistance and mechanical properties. The resulting polybenzimidazoles are therefore limited to use such as bulk and film. Thus, there have been very few reports on polybenzimidazole particles [15]. Brock et al. reported the preparation of polybenzimidazole beads using a non-aqueous

Y. Yoshioka (✉) · K. Asao
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

suspension method with a series of surface-active suspension stabilizers. The average particle size of these beads was 106 μm. However, there have been no reports of nano-sized polybenzimidazole particles.

Carbon materials have excellent electrical properties and thermal conductivity. These types of materials have been extensively investigated because characteristic features depend strongly on the methods of preparation and the resultant morphologies [16–18]. Thus, nano-sized polybenzimidazole and carbon particles with narrow size distributions are expected to be useful in novel applications because of their unique characteristic features and morphologies.

Recently, polybenzimidazole and carbon particles have been prepared from poly(amino-amide) particles. The poly (amino-amide) particles were prepared in an acetone and water solution at 0°C for 20 min and further transformed into the polybenzimidazole and carbon particles by performing dry heat treatments. The obtained particles were spherical nano-sized particles with narrow size distributions. In the current work, we report characteristic features of these particles and investigate their changes in the particles upon exposure to heat. Further, the particles are compared with other particles consisting of a different acid chloride but the same amine compound.

Experimental

Materials

p-Phthalyl chloride, 4,4′-diphenyldicarbony chloride, and 3,3′-diaminobenzidine were purchased from Tokyo Kasei Co. (Japan). Acetone, from Kishida Chemical Co. Ltd. (Japan), was used as the polymerization solvent for the preparation of poly(amino-amide) particles. All reagents were used as received, without any further purification.

Particle preparation

Poly(amino-amide) particles

p-Phthalyl chloride (0.0005 mol) and 3,3′-diaminobenzidine (0.0005 mol) were each dissolved in 50 ml acetone. A quantity of 3 ml distilled water was added to the 50 ml of 3,3′-diaminobenzidine solution, followed by addition of the entire *p*-phthalyl chloride solution at once [19, 20]. The solution was subjected to ultrasonic irradiation at 28 KHz in an ice water bath while mixing for 20 min. The product was extracted by centrifugal separation and washed five times with acetone and water to purify the product from any unreacted monomer. The sample was then dried in a vacuum oven at 100 °C for 3 h and at room temperature for 1 day. The poly(amino-amide) particles were prepared in a similar manner for the 4,4′-diphenyldicarbonyl chloride and 3,3′-diaminobenzidine system.

Polybenzimidazole particles

Poly(amino-amide) particles were heated in a nitrogen atmosphere using the thermal program on the TG/DTA analyzer, as described in the results and discussion section. The poly(amino-amide) particles consisting of *p*-phthalyl chloride and 3,3′-diaminobenzidine were transformed into poly(*p*-phenylenebenzimidazole) particles, and the poly (amino-amide) particles consisting of 4,4′-diphenyldicarbony chloride and 3,3′-diaminobenzidine were transformed into poly(4,4′-diphenylenebenzimidazole) particles.

Carbon particles and materials

The two types of polybenzimidazole particles, poly(*p*-phenylenebenzimidazole) and poly(4,4′-diphenylenebenzimidazole), were heated under a nitrogen atmosphere using the thermal programs on the TG/DTA analyzer, as described in the results and discussion section, in order to obtain carbon particles and materials.

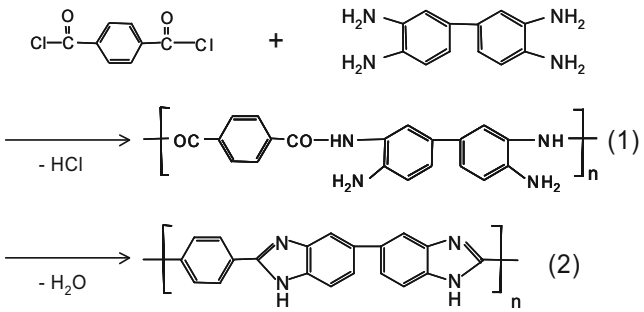
Characterization

IR spectra of the samples were measured using a PerkinElmer Spectrum One infrared spectrometer (PerkinElmer Ltd., USA) in KBr pellets at a resolution of 4 cm^{-1}. The morphologies of the samples were investigated using a Hitachi Fe-SEM S-4700 scanning electron microscope (SEM; Hitachi Ltd., Japan) after sputter depositions with a gold coating. Particle size distribution was measured in a water dispersion using a Photal ELS-8000 Laser Zeta potential analyzer (Otsuka Electronics Ltd., Japan). X-ray diffraction profiles were obtained using a Rigaku RINT-2500 X-ray diffractometer (Rigaku Ltd., Japan) with graphite monochromatized Cu-Kα radiation and a scan speed of 1° min^{-1}. The thermal properties of the samples were measured in a nitrogen atmosphere, using a SII Nano Technology TG/DTA 6300 analyzer (SII Nano Technology Inc., Japan).

Results and discussion

Characteristic features of poly(amino-amide) particles

Poly(amino-amide) was prepared according to the reaction shown in Scheme 1(1). Figure 1a shows the infrared spectrum of the poly(amino-amide) obtained in the region of 500–4000 cm^{-1}. The poly(amino-amide; PAA) prepared from a *p*-phthalyl chloride (PPC) and 3,3′-diaminobenzidine sample is referred to as PPC–PAA. Characteristic



Scheme 1 Poly(*p*-phenylenebenzimidazole) prepared in two steps containing ring-closing reactions of poly(amino-amide)

bands due to polyamide were observed: for example, 3,241 cm^{-1} [amide A (N–H stretching mode)], 1,650 cm^{-1} [amide I (C—O stretching mode)], and 1,520 cm^{-1} [amide II (coupling of C–N stretching and N–H in-plane bending modes)]. In addition, a strong band next to the amide A band at 3,241 cm^{-1} was detected at 3,347 cm^{-1}, corresponding to the N–H stretching mode of the amino groups (–NH_2) [21]. Thus, it is speculated that the obtained sample was poly (amino-amide).

Figure 2a shows a SEM image of the PPC–PAA sample. As can be seen in the image, the particles are spherical with a narrow size distribution. Figure 3a shows the histogram of the size distribution of the particles in a water dispersion. The average diameter with standard deviation was estimated to be 241±51 nm.

Transformation from poly(amino-amide) to poly(*p*-phenylenebenzimidazole) particles

Heat treatments of obtained poly(amino-amide; PPC–PAA) particles were performed under various processing temperatures and times under a nitrogen atmosphere in order to prepare poly(*p*-phenylenebenzimidazole). The sample was dried in a vacuum oven at 100 °C for 3 h and then at room temperature for 1 day. The sample was then kept under nitrogen at 100 °C for 1 h before heat treatment in order to eliminate the moisture that had absorbed to PPC–PAA particles. The sample was heated from 100 °C to the preset temperature at a rate of 10 °C/minute, and held at the preset temperature for the set time, using the TG/DTA analyzer. The product labeled PPC-300C3H indicates that the PPC–PAA sample was heated to 300 °C and held at 300 °C for a time period of 3 h.

Dependence on processing temperature

Infrared spectra

Figure 1b–f shows the infrared spectra of PPC-300C3H, PPC-335C3H, PPC-350C3H, PPC-370C3H and PPC-380C3H obtained by heat treatments, respectively. The spectra changed remarkably as the processing temperature increased. The intensities of the –NH_2 band at 3,347 cm^{-1}, the amide I band at 1,650 cm^{-1} and the amide II band at 1,520 cm^{-1} decreased gradually, whereas characteristic bands due to imidazole rings emerged at 1,380 cm^{-1} (C–N stretching mode), 1,450 cm^{-1} (C–N in-plane mode), 1,610 cm^{-1} (C—C, C—N ring stretching mode), 3,154 cm^{-1} ('free' non-hydrogen-bonded N–H stretching mode) and 3,400 cm^{-1} (self-associated N–H stretching mode) and increased gradually [8, 21, 22]. This suggests that ring-closing reactions occurred, that is, poly(amino-amide) changed to poly(p-phenylenebenzimidazole) upon heat treatment, as shown in Scheme 1(2). The ratio of ring-closing, that is, the number ratio of imidazole rings generated after heat treatment to amino-amide units existing in poly(amino-amide) before heat treatment increased as the processing temperature increased. The infrared spectrum of the PPC-370C3H sample showed a disappearance of the amide I band at 1,650 cm^{-1} (C—O stretching mode) (Fig. 1e). Further, the infrared spectrum of the PPC-370C3H sample was identical to that of the PPC-380C3H sample (Fig. 1e, f). Thus, it can be inferred that the poly (amino-amide) particles were transformed completely into poly(*p*-phenylenebenzimidazole) upon heat treatment at 370 °C for 3 h.

X-ray

Figure 4a–e show X-ray diffraction patterns of PPC–PAA, PPC-300C3H, PPC-335C3H, PPC-350C3H and PPC-370C3H samples, respectively. The pattern of PPC–PAA showed a broad peak, indicating the degree of crystallinity is amorphous. The peaks were almost the same in spite of the processing temperatures. Thus, it is speculated that the degree of crystallinity did not depend on the processing temperature.

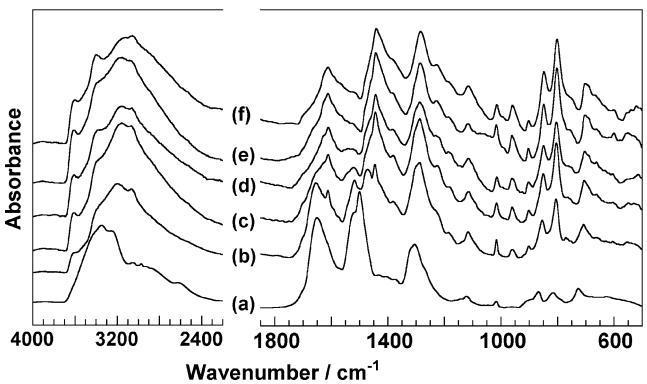


Fig. 1 Infrared spectra in the region of 500–4,000 cm^{-1}. (*a*) PPC–PAA, (*b*) PPC-300C3H, (*c*) PPC-335C3H, (*d*) PPC-350C3H, (*e*) PPC-370C3H, (*f*) PPC-380C3H

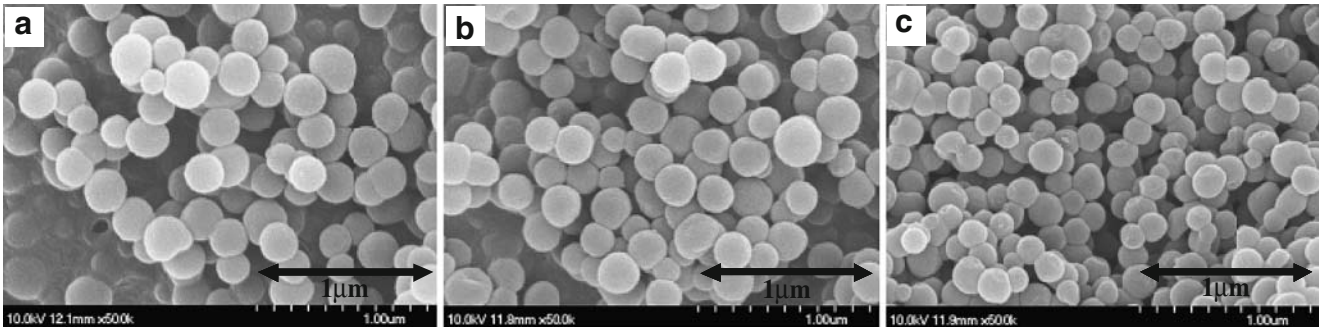


Fig. 2 SEM images: **a** PPC–PAA, **b** PPC-370C3H, **c** PPC-370C3H-CM

TG/DTA

Thermogravimetric (TG) and differential thermal analyses (DTA) of PPC–PAA, PPC-300C3H, PPC-335C3H, PPC-350C3H and PPC-370C3H samples were carried out in the temperature region of 100–1,000 °C, using a TG/DTA analyzer. These samples were dried in a vacuum oven at 100 °C for 3 h and then at room temperature for 1 day, and kept in a nitrogen atmosphere at 100 °C for 1 h prior to measurements in order to remove the adsorbed moisture. Figure 5a–e show the corresponding thermal diagrams for each of the samples.

The TG curve changed significantly for PPC–PAA at three steps, ca 200 °C, 360 °C, and 580 °C. On the other hand, the DTA curve showed a broad exothermic peak over the measurement temperature region. The onset temperatures for weight loss of the PPC-300C3H–PPC-370C3H samples increased as the processing temperatures of heat treatments increased. That is, the temperatures at which weight loss began were 360 °C for PPC-300C3H, 380 °C for PPC-335C3H, 395 °C for PPC-350C3H, and 429 °C for PPC-370C3H. On the other hand, the number ratios for the ring-closing of PPC-300C3H–PPC-370C3H samples increased as the processing temperatures increased, as shown in the infrared spectra. Thus, the temperature at which weight loss begins is thought to be an indicator of the number ratio of ring-closings in the poly(amide-benzimidazole) sample. The temperature at which weight loss of the poly(*p*-phenylenebenzimidazole) begins in the current work was found to be 429 °C, which temperature was in good agreement with that of poly(*p*-phenylenebenzimidazole) reported previously [3]. The temperature at which weight loss begins was also estimated to be 429 °C for PPC-370C3H. Furthermore, based on the results of the thermal diagrams and infrared spectra, it is speculated that the weight loss in the temperature region of 100–370 °C is derived from the evaporation of H_2O generated in the ring-closing reactions, as shown in Scheme 1(2).

Dependence on processing time

The influence of the processing times for heat treatments was evaluated for the ring-closing reactions. Initially, the heat treatments were performed at 370 °C for various processing times. The temperature at which the onset of weight loss was observed was estimated for the samples to be; 410 °C for PPC-370C1H, 421 °C for PPC-370C2H, 429 °C for PPC-370C3H, 428 °C for PPC-370C4H, 429 °C for PPC-370C5H, and 429 °C for PPC-370C6H. Similarly, heat treatments were performed at 300 °C for various processing times. The temperature at which the onset of weight loss was observed was estimated to be; 355 °C for PPC-300C1H, 360 °C for PPC-300C2H, 360 °C for PPC-300C3H, 360 °C for PPC-300C4H, 361 °C for PPC-300C5H, and 360 °C for PPC-300C6H. Based on these results, in the cases in which the processing times were greater than 2 h, the temperature at which the onset of weight loss began was certain; either 360 or 429 °C.

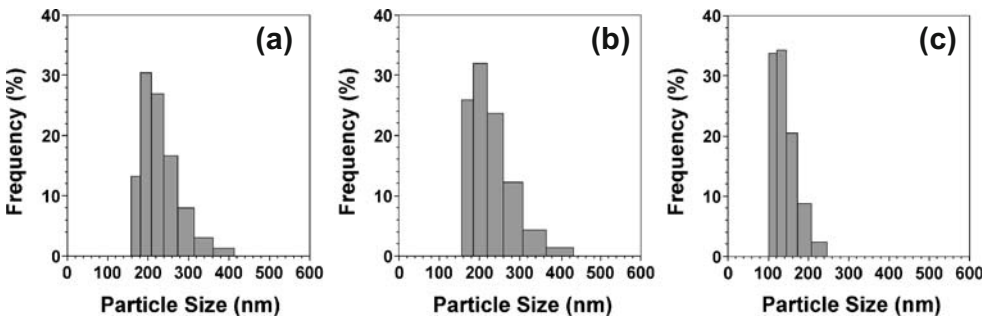


Fig. 3 Histograms of particle size distribution: **a** PPC–PAA, **b** PPC-370C3H, *c* PPC-370C3H-CM

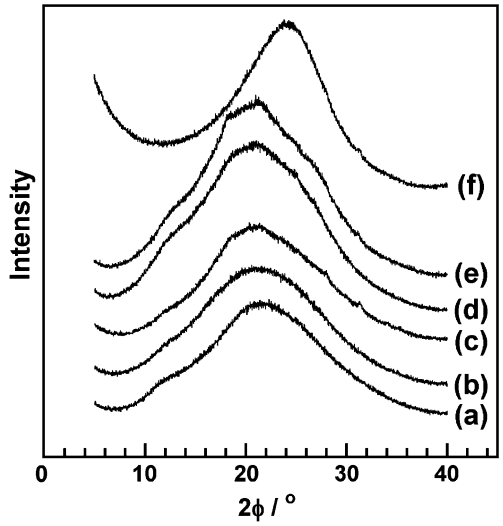


Fig. 4 X-ray diffraction patterns: (*a*) PPC–PAA, (*b*) PPC-300C3H, (*c*) PPC-335C3H, (*d*) PPC-350C3H, (*e*) PPC-370C3H, (*f*) PPC-370C3H-CM

Moreover, the same results were observed in the infrared spectra of these samples (not shown). Thus, it is speculated that the ring-closing reactions do not proceed at a certain processing temperature, even if the processing time is over 2 h. The proper processing time for this heat treatment was therefore estimated to be 3 h.

Based on the results of variable processing times and temperatures, the ring-closing reactions were determined to depend more strongly on the processing temperature than the processing time. The proper and effective processing temperature and time of heat treatment for the transformation from poly(amino-amide) to poly(*p*-phenylenebenzimidazole) were determined to be 370 °C for 3 h.

Characteristic features of poly(*p*-phenylenebenzimidazole) particles

Figure 2b shows a SEM image of the obtained poly(*p*-phenylenebenzimidazole; PPC-370C3H sample). As can be seen in the image, the particles are spherical. Figure 3b shows the histogram of size distribution of these particles in a water dispersion water. The average diameter and standard deviation were estimated to be 241±60 nm, respectively. Compared with the diameters of poly(*p*-phenylenebenzimidazole) particles estimated from the SEM image and by the histogram of size distribution, these values were almost same. Therefore, it is said that the heat treatment did not result the connections among the particles. On the other hand, the average diameter of the particles after the heat treatment (poly(*p*-phenylenebenzimidazole) particles) was almost same as that of the particles before the heat treatment (poly(amino-amide) particles), 241 nm, indicating that the heat treatment did not have a remarkable influence on the diameter and surface morphology of the particles.

Characteristic features of carbon particles

The products obtained after the heat measurement in the temperature range of 100–1,000 °C (Fig. 5) were carbon materials. This was supported by the infrared spectra of them (not shown). That is, the spectra were corresponding not to polybenzimidazole but to carbon. For example, the product labeled PPC-370C3H-CM suggests that the PPC-370C3H sample was heated to 1,000 °C to in order to obtain a carbon material. The residue percentages at 1,000 °C for the PPC-300C3H-CM–PPC-370C3H-CM samples were 59–68% (Fig. 5).

Figure 2c shows a SEM image of the obtained PPC-370C3H-CM. Further, the images show that the obtained particles were spherical particles. Figure 3c shows the histogram of size distribution of these particles in a water dispersion. The average particle diameter and standard deviation were estimated to be 151.2±33.1 nm, respectively. The average particle diameter was almost the same as the diameter estimated from the SEM image, indicating that the particles did not combine. The average particle diameter

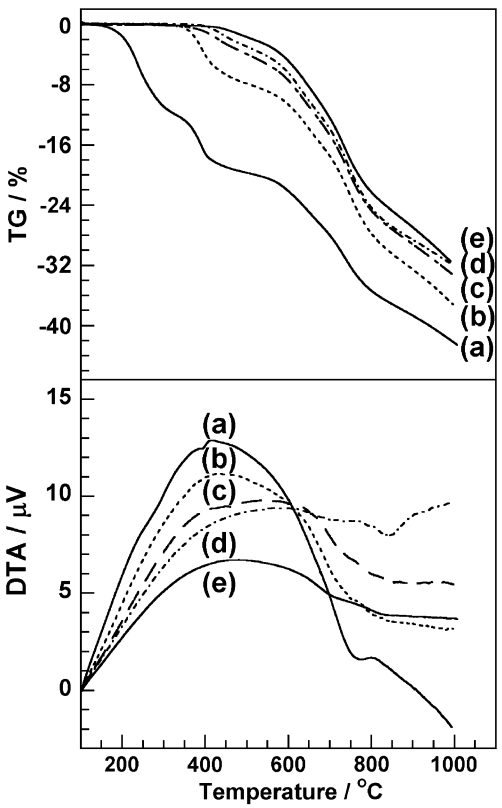
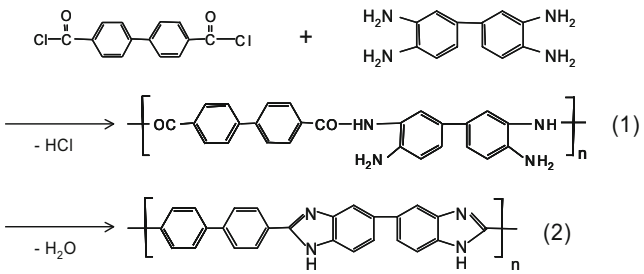


Fig. 5 Thermal diagrams in the temperature range of 100–1,000 °C estimated from the TG/DTA measurements for (*a*) PPC–PAA, (*b*) PPC-300C3H, (*c*) PPC-335C3H, (*d*) PPC-350C3H, (*e*) PPC-370C3H



Scheme 2 Poly(4,4′-diphenylenebenzimidazole) prepared in two steps containing ring-closing reactions of poly(amino-amide)

of the carbon particles was ca. 63% shorter than that of the precursor poly(*p*-phenylenebenzimidazole) particles (PPC-370C3H). On the other hand, the coefficients of variation of the PPC-370C3H and PPC-370C3H-CM samples were almost the same; 25% and 22%, respectively. Thus, it is speculated that PPC-370C3H-CM particles were obtained by homogeneous shrinkage of PPC-370C3H particles. Furthermore, the average diameters of the PPC-300C3H-CM–PPC-370C3H-CM particles were the same in spite of the number ratios of the ring-closing reaction of the precursors (PPC-300C3H–PPC-370C3H samples).

Figure 4f shows the X-ray diffraction pattern of PPC-370C3H-CM. The pattern was different from that of the poly(*p*-phenylenebenzimidazole) particles (PPC-370C3H particles).

Comparison between poly(*p*-phenylenebenzimidazole) and poly(4,4′-diphenylenebenzimidazole)

Poly(amino-amide) particles consisting of 4,4′-diphenyldicarbony chloride and 3,3′-diaminobenzidine, which have the same amine but a different acid chloride, were prepared in the similar manner (Scheme 2(1)). The poly(amino-amide) product obtained was labeled DPC–PAA. This sample was compared with the PPC–PAA sample as far as morphology and characteristic features.

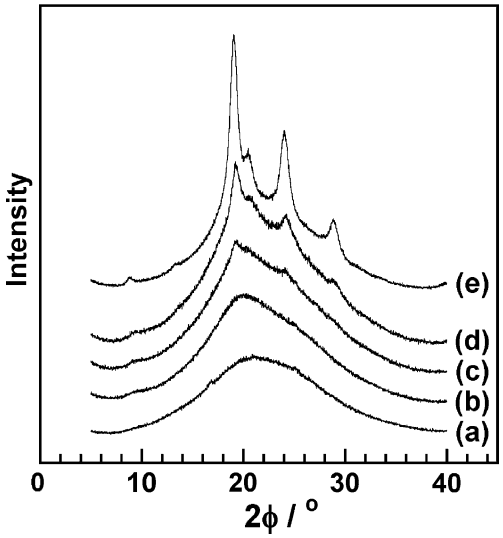


Fig. 7 X-ray diffraction patterns: (*a*) DPC–PAA, (*b*) DPC-300C3H, (*c*) DPC-330C3H, (*d*) DPC-345C3H, (*e*) DPC-360C3H

Figure 6a shows a SEM image of the DPC–PAA sample. The image confirms that the spherical particles had a narrow size distribution. The average particle diameter and standard deviation of the particles were estimated to be 292± 44 nm, using the size distribution histogram. The average diameter of DPC–PAA was significantly longer than that of PPC–PAA (241 nm). The difference in these diameters is thought to be related to the miscibility between the particle and the reaction solution.

The DPC–PAA sample was heated using a TG/DTA analyzer at various processing temperatures for 3 h to obtain poly(4,4′-diphenylenebenzimidazole) particles (Scheme 2(2)). The infrared spectra and thermal diagrams of the obtained products suggest that the proper processing temperature of heat treatment was estimated to be 360 °C. Figure 6b shows a SEM image of the DPC-360C3H sample. The temperature at which the weight loss of the DPC-360C3H sample began was estimated to be 425 °C. Thus, the proper processing temperature and the temperature

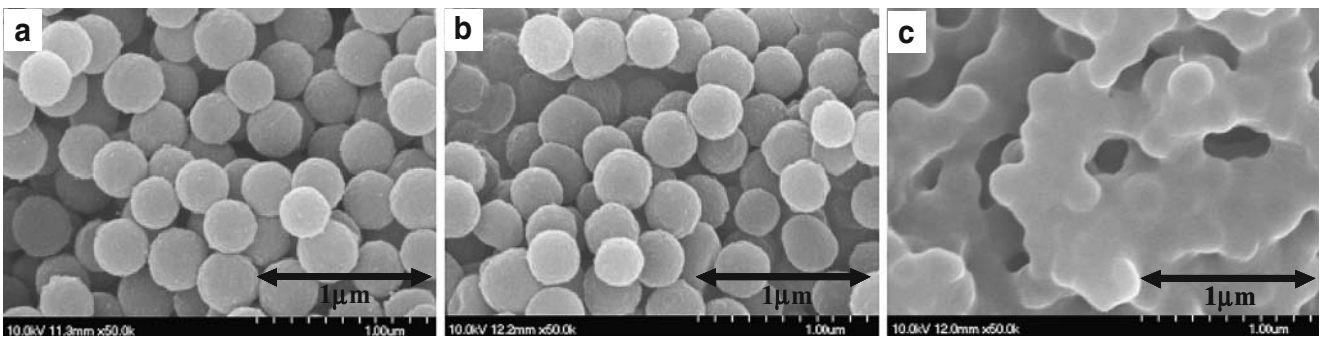


Fig. 6 SEM images: **a** DPC–PAA, **b** DPC-360C3H, **c** DPC-360C3H-CM

at which weight loss began were consistent with those for the PPC-370C3H sample. The average diameter with standard deviation of the DPC-360C3H particles was 284±51 nm, which was consistent with the precursor DPC–PAA particles. Thus, heat treatment did not seem to have a significant influence on the diameter and surface morphology of the particles. The same result was observed for poly(*p*-phenylenebenzimidazole).

Figure 7a–e shows the X-ray patterns of DPC–PAA, DPC-300C3H, DPC-330C3H, DPC-345C3H and DPC-360C3H products obtained by the heat treatment at various processing temperatures. As the processing temperature increased, one broad peak gradually became several sharp peaks, indicating that the degree of crystallinity increased. This change was remarkable compared with the change observed for the PPC–PAA–PPC-370C3H samples (Fig. 4a–e). The difference in the degree of crystallinity between the PPC-370C3H and DPC-360C3H samples is thought to be related to the difference in the chemical structures. That is, PPC–PAA bears one phenylene group whereas DPC–PAA bears two phenylene groups in the diacid chloride side. The chemical structure is essentially the same for the amine moiety. Thus, the difference in the degree of crystallinity is thought to be related to the difference in the structure of the diacid chloride side; namely, the phenylene groups. The ring-closing reaction progresses upon heat treatment and the conformation of the molecular chain changes significantly with the change in chemical structure. The change in conformation is induced not only for the imidazole moiety, but also for the phenylene groups [9]. The two phenylene groups for DPC–PAA are thought to generate a stronger van der Waals force for intermolecular interactions than the one phenylene group on PPC–PAA. In addition, the density of intermolecular hydrogen bonds between N–H···N on the imidazole in the molecular sheets of DPC–PAA is lower than that of PPC–PAA. Thus, it is speculated that the change in conformation of DPC–PAA is easier upon heat treatment. Thus, the crystal packing of the molecular chains of DPC–PAA changes more significantly and there is a higher degree of crystallinity.

Comparing the morphologies of the carbon products obtained by the heat measurements in the temperature range of 100–1,000 °C, the PPC-370C3H-CM product was in the particulate form, whereas the DPC-360C3H-CM product was in bulk (Fig. 6c). This difference is influenced by a number of factors such as the surface charge on the particle and the interaction among the particles. However, details explaining this difference remain unclear at present. The X-ray diffraction pattern of DPC-360C3H-CM, however, was the same to that of PPC-370C3H-CM (Fig. 4f), indicating the same degree of crystallinity. Furthermore, the residual percentage of DPC-360C3H-CM at 1,000°C was 71%.

Conclusions

The poly(amino-amide) particles consisting of *p*-phthalyl chloride and 3,3′-diaminobenzidine and the poly(amino-amide) particles consisting of 4,4′-diphenyldicarbonyl chloride and 3,3′-diaminobenzidine were determined to be spherical particles, with average diameters of 241 nm and 292 nm, respectively. The former was transformed into poly(*p*-phenylenebenzimidazole) and the later was transformed into poly(4,4′-diphenylenebenzimidazole) by heat treatments. The onset of weight loss due to heat treatment was determined to be 429 °C and 425 °C, for poly(*p*-phenylenebenzimidazole) and poly(4,4′-diphenylenebenzimidazole), respectively. The morphologies and diameters of these polybenzimidazole particles were identical to those of the precursor, poly(amino-amide) particle. However, the number ratio of ring-closing of the obtained products depended on the processing temperature of the heat treatments. Poly(*p*-phenylenebenzimidazole) particles were amorphous and poly(4,4′-diphenylenebenzimidazole) particles had a high degree of crystallinity. Further these poly(*p*-phenylenebenzimidazole) and poly(4,4′-diphenylenebenzimidazole) particles were transformed into carbon materials by the heat measurements up to 1,000 °C. The former consisted of spherical particles with the average diameter of 151 nm and the later was achieved in bulk. The obtained poly(amino-amide), polybenzimidazole and carbon particles showed narrow size distributions.

These particles are expected to be useful for a number of applications, as they are considered nano-sized spherical particles with narrow size distributions and further show excellent and unique characteristic features and functions. The methods used to prepare the particles herein are attractive in that the particles do not contain impurities such as the condensation agents and the reaction solvents used.

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.

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