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Preparation and characterization of nanoscale aromatic polyamide particles

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Abstract

Aromatic polyamide particles were prepared by reacting *m*-phthalyl chloride and 4,4′-diaminodiphenyl ether in a dioxane solution with high water content using a precipitation polymerization method. These nanoscale particles were spherical with a narrow size distribution. The morphologies and characteristic features of the polyamide products obtained depended strongly on the water content of this polymerization system. The characteristic features of the polyamide products were correlated with the amount of HCl (generated during polycondensation) complexed with polyamide products. Water was essential for the formation of spherical particles and played an important role in determining the polarity of the reaction solution. Further, water removed HCl from this condensation reaction system and played an important role as a reaction accelerator.

Keywords: Nanoparticles; Aromatic polyamide; Precipitation polymerization

1. Introduction

Polyamides are common multipurpose synthetic polymers used in a wide range of industrial settings and consumer products. They can be classified into two main families: aliphatic and aromatic polyamides. These materials have excellent mechanical properties [1,2], thermal properties [3−5], and chemical resistance [6,7]. In these respects, aromatic polyamides are superior to aliphatic polyamides. For this reason, there have recently been several detailed studies of aromatic polyamides [8−11]. However, chemically resistant polyamides are insoluble in conventional solvents but soluble in strong acids such as sulfuric acid and hydrochloric acid. These characteristics make it difficult to mold polyamide materials in secondary processes.

Recently, polymer particles with a narrow particle size distribution have received much attention for possible new applications, such as spacers for display, medical carriers, and chromatographic media [12−17]. There have been many reports on nanoscale polystyrene and polymethylmethacrylate particles and their methods of preparation [18−22]. Micrometer-scale aliphatic polyamide particles (e.g. nylon particles) with a narrow particle size distribution [12,23−28] and microcapsules of aromatic polyamides [29−31] have previously been reported. In many of these preparation methods, aliphatic polyamides dissolved in formic acid or *m*-cresol are induced to undergo phase separation by lowering the solution temperature or by gradually adding more solvent [25−28]. However, there have been no reports on nanoscale aromatic polyamide particles with a narrow particle size distribution. These particles, which have excellent mechanical and thermal properties and chemical resistance, are expected to be suitable for various new applications.

Recently, we discovered a new method for fabricating nanoscale aromatic polyamide particles by precipitation polymerization using ultrasonic irradiation [32]. A diamine and a diacid chloride underwent a condensation reaction in a dioxane or an acetone solution containing a considerable volume of water, resulting in the formation of aromatic polyamide particles with various surface morphologies. However, as condensation reactions are generally carried out in anhydrous solvents, it was considered important to clarify the reaction mechanism in detail. Thus, the characteristic features of polyamide products obtained under various reaction conditions

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were estimated by using diverse analytical methods such as thermal analysis, infrared spectroscopy, and gel permeation chromatography. The aromatic polyamide particles used in this study were soluble in solvents used for gel permeation chromatography, whereas the aromatic polyamide particles previously obtained were insoluble in these solvents. Therefore, more detailed information concerning the reaction mechanism may be obtained.

In this paper, we focus primarily on the correlation between the characteristic features of the particles and the water content of this reaction system, and examine the reaction mechanism. In addition, in order to obtain more information on the reaction mechanism, we compare this system with the reaction system used in our previous work for preparing aromatic polyamide particles with different morphologies [32].

2. Experimental

2.1. Materials

m-Phthalyl chloride was purchased from Tokyo Kasei Co. (Japan) and 4,4′-diaminodiphenyl ether was purchased from Wakayama Seika Co. (Japan). Dioxane, from Kishida Chemical Co. Ltd. (Japan), was used as the polymerization reaction solvent. These compounds and solvent were used as received, without any further purification.

2.2. Particle preparation

m-Phthalyl chloride (0.0005 mol) and 4,4′-diaminodiphenyl ether (0.0005 mol) were each dissolved in 50 ml dioxane. Distilled water was added in varying amounts (0–50 ml) to the 50 ml of 4,4′-diaminodiphenyl ether solution, followed by addition of the entire *m*-phthalyl chloride solution at once. The solution was subjected to ultrasonic irradiation at 28 kHz in a water bath during this mixing and for a period of 20 min thereafter. The product was extracted by centrifugal separation and washed five times with acetone, dioxane and water to purify the product of any unreacted monomer. The sample was then dried overnight in a vacuum oven at 100 °C.

2.3. 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 Ltd., Japan). Particle size distribution was measured in a water dispersion using a Photal ELS-8000 Laser Zeta potential analyzer (Otsuka Electronics Ltd., Japan). Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out using a SII Nano Technology TG/DTA 6300 analyzer (SII Nano Technology Inc., Japan) by heating the samples in a nitrogen atmosphere at a rate of 10 °C/min. The IR spectra of the samples were measured using a Perkin–Elmer Spectrum One infrared spectrometer (Perkin–Elmer Ltd., USA) in KBr pellets at a resolution of 4 cm^{-1}. Gel permeation chromatography was carried out using a TOSOH GPC-8020 (TOSOH Ltd., Japan) equipped with a TriSEC Model 302 W (Viscotek Ltd., USA) in dimethylformamide containing 40 mM phosphoric acid and 20 mM lithium bromide at a flow rate of 0.6 ml/min and a temperature of 40 °C. The viscosities of the samples were measured using an Ubbelohde viscometer in concentrated sulfuric acid at a temperature of 25 °C. The intrinsic viscosity (η) was obtained from the linear best fit of η_{sp}/c data (η_{sp}: reduced viscosity, c: weight concentration (g/dL)) as a function of the weight concentration (c).

3. Results and discussion

3.1. Morphology

The influence of the water content of this reaction system on the morphology of the polyamide obtained was investigated. The volume of water added varied from 0 to 50 ml for a total of 100 ml dioxane solution (i.e., 50 ml 4,4′-diaminodiphenyl ether solution and 50 ml *m*-phthalyl chloride solution). SEM photographs of some of the products (PA-w0–PA-w33) are shown in Fig. 1(a)–(g). In our notation, the polyamide product labeled as PA-w9, for example, was prepared in a reaction solution containing 10 ml water, that is, with a water content of 9 wt%. The morphology of these products depends on the water content of the reaction mixture. The product prepared in an anhydrous reaction solution, PA-w0, was not obtained in particulate form (Fig. 1(a)), but the products (PA-w9–PA-w29) prepared in a reaction solution containing water were spherical, as shown in Fig. 1(c)–(f). Based on these results, it was concluded that the addition of water to this reaction system was essential for the formation of spherical particles.

The average diameter of these particles decreased from ca. 800 to 200 nm as the water content increased (Fig. 1(c)–(f)). Thus, the average diameter was strongly influenced by the water content. A more detailed examination of particle interconnection was conducted for some products, in which the particle size distribution histogram was measured and the level of interconnection was estimated based on the ratio of the number of interconnected particles to 100 particles used for the particle size distribution measurement (the proportion of interconnected particles). The particle interconnection was evaluated by the comparison between the result of the particle size distribution histogram and the average diameter of particles estimated from SEM images of 100 particles selected at random. For example, for PA-w29, the interconnected particles were not detected; in other words, the particles were well-separated. That is, the diameters of particles obtained by the particle size distribution measurement were in excellent agreement with the average diameter of particles estimated from the SEM images (Fig. 2). The average diameter and its standard deviation were estimated to be ca. 273 nm and 71 nm, respectively, by the particle size distribution measurement. In contrast, for the other products, the interconnection between particles was present in a greater or lesser extent. Thus, the use of a reaction system with optimal water content resulted in the formation of well-separated spherical particles. In other products, the particles showed some interconnection

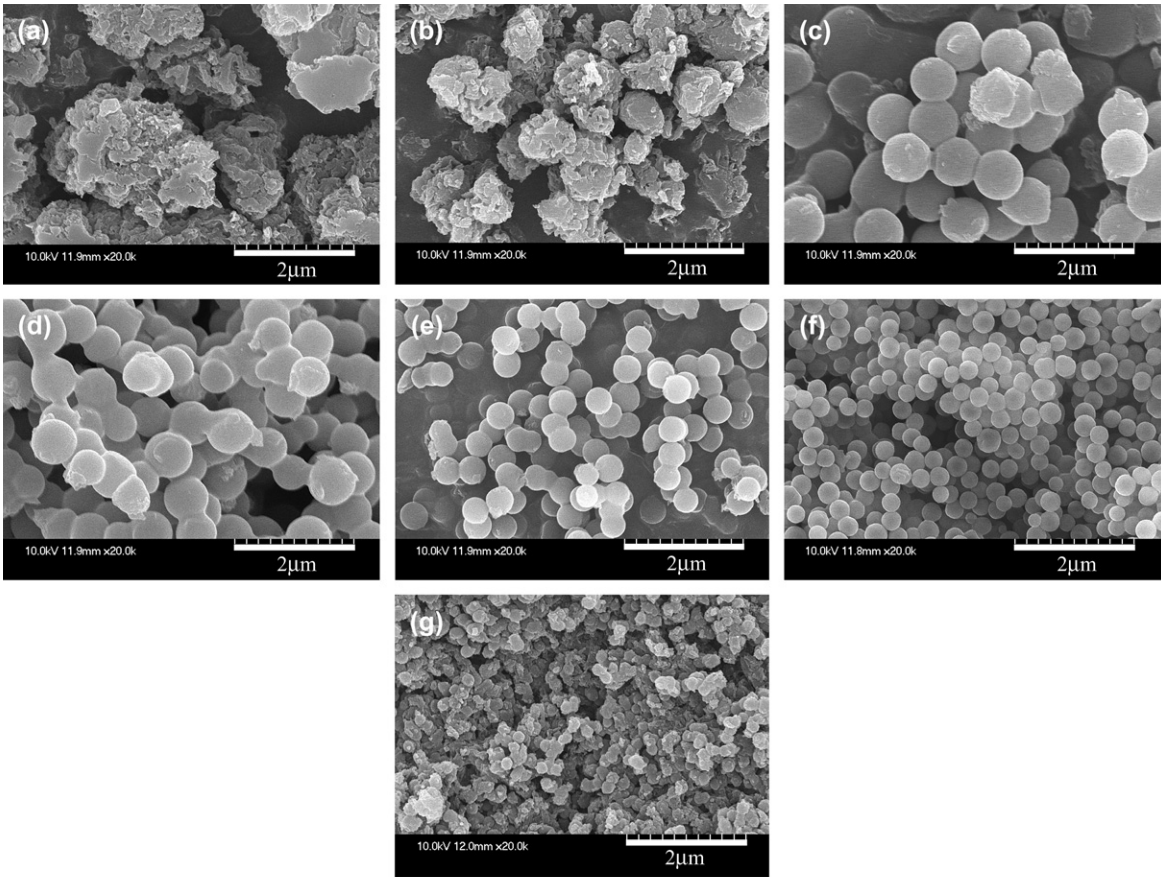

Fig. 1. SEM photographs of polyamide products. Water content: (a) 0 wt%, (b) 5 wt%, (c) 9 wt%, (d) 17 wt%, (e) 23 wt%, (f) 29 wt% and (g) 33 wt%.

even though they were spherical. This tendency may be correlated with the dispersion stability of particles in the reaction solution or the precipitation mechanism of the particles. Accordingly, it can be said that the level of particle interconnection depends on the water content.

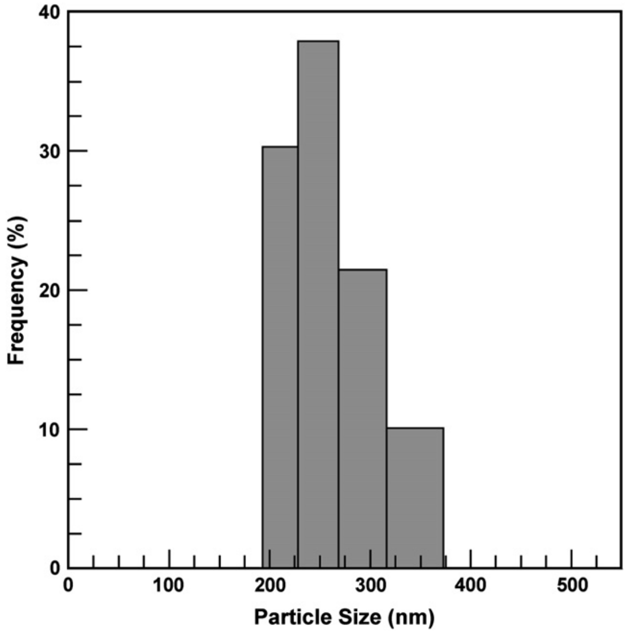

Fig. 2. Particle size distribution histogram.

In addition to particle interconnection, the water content was found to have a strong influence on particle formation and the average particle diameter, as described earlier. The addition of water, a highly polar solvent, exerts a pronounced effect on the polarity of the entire reaction solvent. Therefore, it was speculated that the formation of particles was correlated with the polarity of reaction solvent. Based on these results, we concluded that water can play a useful role in adjusting the polarity of the reaction solution in this polymerization system.

3.2. Thermal decomposition temperatures

The influence of the water content on polymer thermal properties was investigated. The thermal decomposition temperatures T_d of PA-w0–PA-w33 at 5 and 10% weight loss were estimated from TG/DTA measurements and plotted against the water contents of the systems in which the polymers were formed (Fig. 3). The T_d at 5% weight loss increased rapidly as the water content increased from 0 to 9 wt%, and then increased more gradually from 9 to 33 wt%. A similar tendency was observed for T_d at 10% weight loss. T_d is conventionally associated with molecular weight [33–35]—although in this case, concrete values of molecular weight

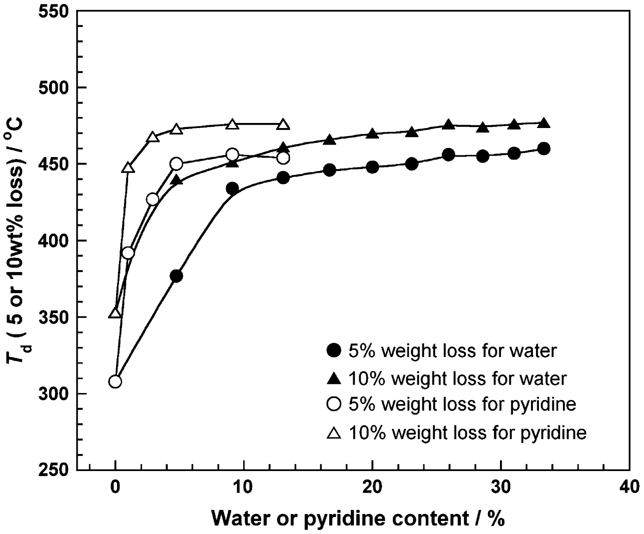

Fig. 3. Plot of T_d (thermal decomposition temperature at 5 or 10% weight loss) against water and pyridine content.

could not be specified—and its value increases in proportion to molecular weight, particularly in the low-molecular-weight region. Consequently, it was thought that the molecular weight of the products increased as the water content of the reaction system increased from 0 to 9 wt%.

Generally, a reaction accelerator such as pyridine is added to condensation reactions between diamines and diacid chlorides to remove HCl generated during polymerization, because HCl hinders the polymerization reaction, resulting in a lower-molecular-weight product. The change induced by the addition of pyridine was compared with reactions using water. T_d values (5 and 10% weight loss) were estimated for products (PA-p0–PA-p13) which were prepared in reaction solutions containing 0, 1, 3, 5, 10 and 15 ml pyridine—that is, 0, 1, 3, 5, 9 and 13 wt% pyridine content, respectively—and the results were plotted against the pyridine contents (Fig. 3). The T_d for 5% weight loss increased rapidly from 0 to 5 wt%, then leveled off and remained almost constant from 5 to 13 wt%. The temperature at this plateau (ca. 455 °C) was almost equal to the values measured for water contents of 17–33 wt%. Similar trends were observed for the T_d at 10% weight loss. The T_d value at 5% weight loss (ca. 455 °C) was in excellent agreement with that of polyamide with the same chemical structure, as reported previously [11]. Thus, the change in T_d resulting from the addition of pyridine was very similar to that seen for water, although the effects were observed at different rates for different amounts of water/pyridine added. Thus, addition of water and pyridine gave similar and significant effects for the reaction system.

3.3. Infrared spectra

In the infrared spectra of the products PA-w0–PA-w33 and PA-p0–PA-p13, characteristic bands due to aromatic polyamides were observed; for example, at 3260 cm^{-1} [amide A (N–H stretching mode)], 1655 cm^{-1} [amide I (C=O stretching mode)], and 1530 cm^{-1} [amide II (coupling of C–N stretching and N–H in-plane bending modes)]. Fig. 4(a) shows the infrared spectra of the products PA-w0–PA-w29 in the 1800–4000 cm^{-1} region. There are two strong bands at ca. 2810 cm^{-1} and 2560 cm^{-1} in the spectrum of the PA-w0 product, corresponding to the hydrochloride salt of an amine (–NH_3Cl) [36]. Based on the characteristic infrared bands due to polyamides and high T_d at 5% weight loss (ca. 308 °C), the PA-w0 product was thought to be not monomeric but a relatively high-molecular-weight polyamide. Thus, it is probable that the amine end-groups of the polyamide were capped with HCl. As shown in Fig. 4(a), these two bands decreased markedly in intensity with increasing water content. Fig. 4(b) shows the infrared spectra of the products PA-p0–PA-p9 in the same region. The changes in these spectra are similar to those shown in Fig. 4(a), that is, the two bands at 2810 cm^{-1} and 2560 cm^{-1} were again significantly weakened as the pyridine content increased.

Next, in order to investigate these changes in detail, the intensity ratio of the amide (–NHCO–) band to the amine

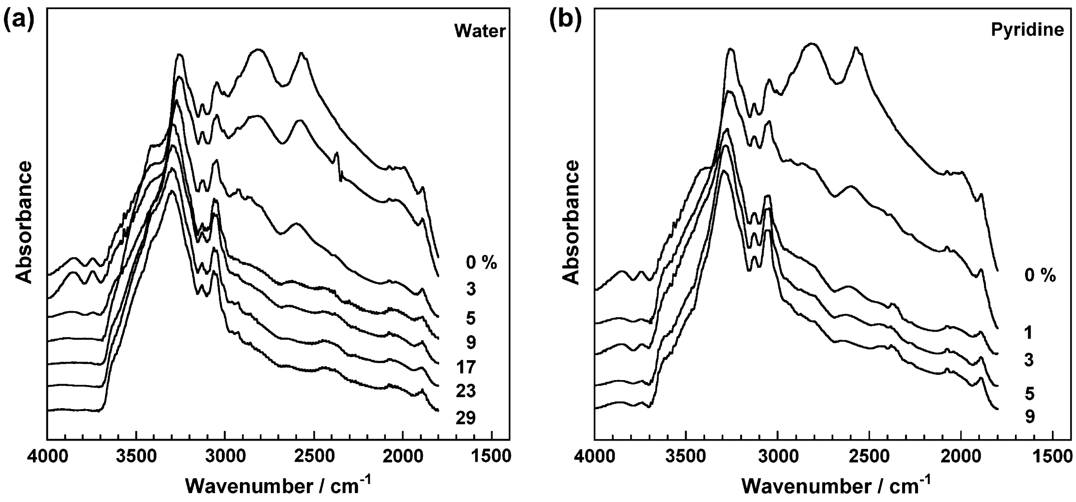

Fig. 4. Infrared spectra in the region 1800–4000 cm^{-1} for (a) PA-w0–PA-w29 and (b) PA-p0–PA-p9.

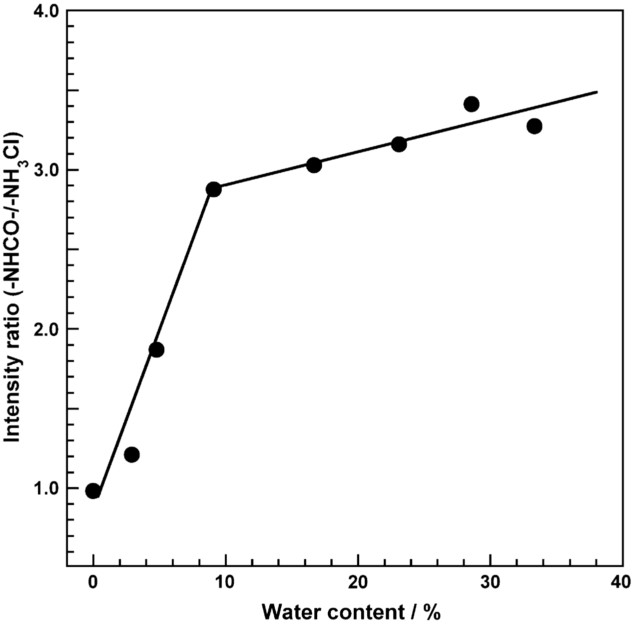

Fig. 5. Plot of intensity ratio of two infrared bands (−NHCO−/−NH$_3$Cl) against water content.

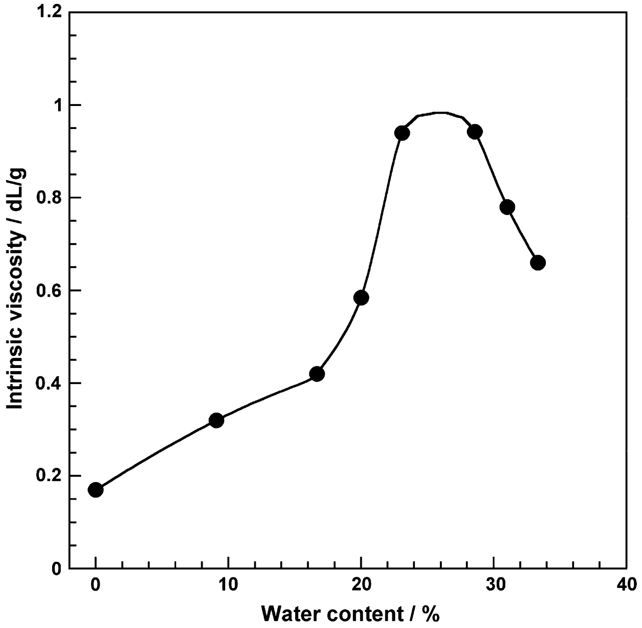

Fig. 6. Plot of intrinsic viscosity against water content.

hydrochloride (−NH$_3$Cl) band was estimated. The intensity of the amide band at 3260 cm^{-1} is correlated with the degree of polymerization [37], whereas the intensity of the amine hydrochloride band at 2560 cm^{-1} is correlated with the amount of amines capped with HCl [36]. Strong absorption in the latter band indicates that many amine groups are capped with HCl, which means that the degree of polymerization is low, as amine groups capped with HCl cannot react further with diacid chloride. Therefore, it may be concluded that a high intensity ratio for these bands (−NHCO−/−NH$_3$Cl) reflects a high degree of polymerization. Both bands shifted gradually to higher frequency as the water content increased; hence, the intensities at the new band positions were used for estimation of the intensity ratio. Fig. 5 shows a plot of the intensity ratio (−NHCO−/−NH$_3$Cl) against water content. The intensity ratio increased rapidly as the water content increased from 0 to 9 wt%, and then increased more gradually from 9 to 33 wt%. The behavior of the intensity ratio in the 0−9 wt% range indicates that the amount of amines capped with HCl decreased as the water content increased, and that the degree of polymerization increased rapidly. Therefore, it may be speculated that water removes HCl from the reaction system, preventing the reaction between diamine and HCl.

3.4. Molecular weight

In order to estimate the molecular weights of the polyamide products, their intrinsic viscosities (η) were measured using an Ubbelohde viscometer with concentrated sulfuric acid. Fig. 6 shows a plot of the resulting intrinsic viscosities (η) against the water contents of the reaction systems. The value of η increased gradually as the water content increased from 0 to 17 wt%, and then rapidly from 17 to 23 wt%; it then remained almost constant from 23 to 29 wt% and decreased gradually from 29 to 33 wt%. Meanwhile, the weight-average molecular weights (M_w) and polydispersities P_d ($=M_w/M_n$) of the polyamide products were estimated by GPC measurements in dimethylformamide; the results are listed in Table 1. The change in M_w with water content was similar to that of η. The M_w of PA-w33 could not be obtained because a fraction of the product was insoluble in dimethylformamide. The reason for this insolubility is currently unknown. The P_d values of PA-w0−PA-w29 were in the range from 1.22 to 2.56, indicating that the polyamide products had relatively narrow molecular weight distributions.

3.5. Reaction mechanism

Based on the foregoing results, the reaction mechanism may be discussed, focusing primarily on the role of water in this reaction system. The change in the intensity ratio of the IR bands representing −NHCO− and −NH$_3$Cl was in excellent agreement with the estimates of T_d obtained from TG/DTA measurements (Figs. 3 and 5). In the range of 0−9 wt% water content, this ratio and T_d increased rapidly, indicating that water was acting to remove the HCl generated from the condensation reaction, greatly accelerating the polycondensation reaction. However, the increase in η over this range

Table 1
Molecular weights (M_w) and polydispersities (P_d) of polyamide products

	M_w (g/mol)	P_d
PA-w0	7640	1.38
PA-w9	12,700	1.22
PA-w17	16,800	1.42
PA-w20	31,100	1.81
PA-w23	71,800	2.56
PA-w29	74,000	2.36

was not as marked as the increase in the 17–23 wt% range. Accordingly, it can be said that in the 0–9 wt% region HCl was only partially removed by the added water, resulting in the formation of low-molecular-weight polyamides. In the 9–23 wt% range, the intensity ratio and T_d increased gradually, while η increased gradually in the range 9–17 wt% and then more rapidly in the 7–23 wt% range. Judging from these results, it is likely that in the 9–17 wt% range a certain amount of HCl was present, inhibiting polymerization and resulting in low-molecular-weight polyamides. In other words, the presence of even tiny amounts of HCl has a marked influence on the characteristic features of the polymer, such as molecular weight. In the 17–23 wt% range, however, it is highly possible that HCl was removed almost entirely, inducing formation of high-molecular-weight polyamides. However, the values of T_d at 5% and 10% weight loss did not change appreciably in this water content range, remaining almost constant (ca. 455 and 475 °C) in spite of the significant increase in η. Previous reports have shown that T_d remains constant for products of high molecular weight above a certain level [38]. In other words, products with the same chemical structure showed almost the same degree of thermal stability above a certain molecular weight. The T_d values at 5% and 10% weight loss were ca. 455 and 475 °C, respectively, which are almost the same as those of high-molecular-weight Kevlar fiber [5,39]. Accordingly, it is speculated that these are the highest T_d values obtainable for aromatic polyamide of this chemical structure, which is mainly composed of amide bond and benzene ring. Further, combined with the results of M_w based on GPC measurements, it is speculated that T_d increases with M_w in the region below ca. 20,000 g/mol, but is constant for M_w above ca. 20,000 g/mol in this system (Fig. 3 and Table 1) [38]. This speculation is supported by the finding that T_d remains constant even when η decreases, that is, even at the lower estimated molecular weight of PA-w33. The molecular weights of the products peaked in the 23–29 wt% water content range, indicating that this is the optimal water content for the condensation polymerization system. Based on these results, it was concluded that water acts as a reaction accelerator, removing HCl from the system and thus accelerating the condensation polymerization reaction, which results in the production of high-molecular-weight polyamides. The decrease in the value of η in the 29–33 wt% range implies that the presence of excessive amounts of water disturbs the condensation reaction.

In general, addition of water is avoided in condensation reactions of this type because water hydrolyzes the acid chloride to a carboxylic acid, inhibiting condensation. However, we reported in a previous paper that in a reaction system of *p*-phthalyl chloride and 4,4′-diaminodiphenyl ether, the acid chloride reacted predominantly with the diamine (condensation reaction) rather than with water (hydrolysis reaction) [32]. The above-described reaction mechanism can be applied to the current reaction system of *m*-phthalyl chloride and 4,4′-diaminodiphenyl ether based on the molecular weights and yields of the products obtained. However, in this study, the presence of excess water was found to promote the formation of products of lower molecular weight. Thus, the water content has a significant influence on the reaction mechanism. It may be concluded that below the optimal water content, the predominant action of water is to accelerate the condensation reaction, while above the optimal water content, the presence of water causes acceleration not only of the condensation reaction but also of the hydrolysis reaction.

3.6. Comparison with previously used reaction system

Based on the reaction mechanism described above, the reaction system used in this study (*m*-phthalyl chloride and 4,4′-diaminodiphenyl ether) was compared with that used in the previous study (*p*-phthalyl chloride and 4,4′-diaminodiphenyl ether), in which the same diamine but a different diacid chloride was used. The former was designated as the PA-*m*-pc system and the PA-w0–PA-w33 products as PA-*m*-pc products. In the same way, the latter reaction system and the resulting products were labeled as the PA-*p*-pc system and PA-*p*-pc products, respectively.

The yields of all PA-*m*-pc products were between 25 and 50%. In contrast, the yields of all PA-*p*-pc products were above 94%, as mentioned in the previous paper. However, although the yields of PA-*m*-pc products were much lower, their intrinsic viscosities were higher than those of the PA-*p*-pc products; for example, the intrinsic viscosity (η) of PA-w29 was 0.93 dL/g, whereas that of the PA-*p*-pc product obtained under the same conditions was 0.40 dL/g. Thus, the PA-*m*-pc products had higher molecular weights than the PA-*p*-pc products, in spite of their lower yields. Accordingly, it is speculated that the low yields of the PA-*m*-pc products are due to miscibility between the reaction solvent and the product rather than reaction inhibition by hydrolysis of the acid chloride. In addition, the morphologies and degrees of crystallinity of the PA-*m*-pc and PA-*p*-pc particles were quite different. The PA-*m*-pc particles were smooth amorphous spheres, whereas the PA-*p*-pc particles were porous spheres with a higher degree of crystallinity. Therefore, it is speculated that the PA-*m*-pc and PA-*p*-pc systems employ the same condensation mechanism for the reaction of diamine and diacid chloride, but have different precipitation mechanisms for particle formation. The mechanism of particle formation will be further discussed in our next paper.

4. Conclusion

Aromatic polyamide particles were prepared by reacting *m*-phthalyl chloride with 4,4′-diaminodiphenyl ether in a dioxane solution with a high water content, using a precipitation polymerization method. The morphology of the polyamide products obtained was found to depend on the water content of this reaction system. The particles prepared in a dioxane solution with 29 wt% water content were spherical, with an average diameter of ca. 273 nm, and had a narrow size distribution. Water was essential for the formation of spherical particles, and played an important role in adjusting the polarity of the reaction solution. The thermal decomposition temperatures

(T_d) and weight-average molecular weights (M_w) of the products also depended strongly on the water content of the reaction system. These results were correlated with the amount of HCl generated during polycondensation, which complexed with the polyamide products. It is thought that water removes HCl from the condensation reaction system, allowing the formation of polyamide products with high molecular weights. Therefore, water plays an important role as a reaction accelerator. The information can be applied for the synthesis of aromatic polyamides and other polymer particles and allow control of their characteristic features and morphologies.

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