

Preparation of Aliphatic Polypyromellitimide Particles by Polycondensation of Nylon-Salt-Type Monomers Derived from Aliphatic Diamines with Diethyl Pyromellitate in Ethylene Glycol

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RUNNING HEAD: Preparation of Aliphatic Polypyromellitimide Particles

Abstract: Polycondensations of nylon-salt-type monomers composed with diethyl pyromellitate and aliphatic diamines with various methylene lengths were performed at 130 °C in ethylene glycol to afford flower-like particles. Before the polycondensation, the salt monomer solution was homogenous. As the polycondensation proceeded, the solution was getting turbid and polyimide particles grew to around 15 μm for 8 h. Further polycondensation broke the particles in small pieces. The polyimide particles showed the distinctive odd-even effect of methylene chain of diamine in both inherent viscosity and crystallinity. The polyimide particles using diamine with even-methylene length had higher crystallinity and lower inherent viscosity than those using diamine with odd-methylene length.

Key Words: Aliphatic-aromatic polyimide, nylon-salt-type monomer, polymer particles, crystallization, ethylene glycol

1. INTRODUCTION

Wholly aromatic polyimides are the most useful super engineering plastics which exhibit excellent thermal, electrical, and mechanical properties, and have been used widely in aerospace, electronics, and other industries. They are generally prepared through a two-step procedure by the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides giving polyamic acids (PAA), followed by cyclodehydration. Semi-aromatic polyimides derived from nylon-salt-type monomers composed with aliphatic diamine and aromatic tetracarboxylic acids or their diesters also exhibited good thermal and mechanical properties [1-4]. Some synthetic methods of semi-aromatic or wholly-aromatic polyimides using nylon-salt-type monomers were reported such as under high pressure condition [4-8] and by microwave-assisted polycondensation [9].

Recently some polyimide particles were also prepared by dispersion polymerization [10], solution polymerization [11-12], and addition of polyimide solution containing a polymeric stabilizer into a precipitant [13-14].

In this article, aliphatic polypyromellitimide particles were prepared using nylon-salt-type monomers derived from diethyl pyromellitate with diaminoalkane. The nylon-salt-type monomers were extremely reactive, producing directly polyimides by solid-state polycondensation under high pressure in a very short reaction time at a temperature around 250°C [8]. We employed ethylene glycol as a polycondensation solvent to prepare polyimide particles. Ethylene glycol has a high boiling point (198 °C) which allowed the polycondensation at high temperature. And that nylon-salt-type monomers are soluble in ethylene glycol, while prepared polyimides are not, leading to the polyimides particles could gradually grow, as the polycondensation proceeded.

Herein we describe the preparation of semi-aromatic polyimide particles from nylon-salt-type monomer in ethylene glycol (Scheme 1). The particle shapes and their crystallinities were investigated using aliphatic diamines having various methylene lengths.

2. EXPERIMENTAL

2.1. Measurements

Scanning electron microscopy (SEM) measurements were conducted using JEOL JSM-588 scanning microscope. Differential scanning calorimetry (DSC) and thermogravimetry were performed with Shimadzu thermal analyzers DSC-41 and ULVAC TGD 9600, respectively. Wide-angle X-ray diffraction patterns were obtained by using a RIGAKU RINT 2000 with Cu K α radiation generated at 40 kV and 30 mA.

2.2. Materials

Pyromellitic dianhydride (PMDA) was sublimed under a vacuum. Ethanol was refluxed in the presence of magnesium and distilled under nitrogen atmosphere. 1,6-Diaminohexane and 1,8-diaminooctane were distilled under a vacuum. Ethylene glycol was distilled under a vacuum in the presence of calcium hydride. Polyvinylpyrrolidone (PVP; K30) was purchased from Wako Pure Chemical Industries, Ltd. Other reagents were obtained commercially and used as received.

A series of nylon-salt-type monomers NSX, where X stands for the number of methylene length in the aliphatic diamine, were prepared by a reported procedure by mixing of 2,5-di(ethoxycarbonyl)terephthalic acid with an aliphatic diamine in

ethanol [5,9].

2.3. Polycondensation of salt monomer (NS8) in ethylene glycol

Into 50 mL of flask, 0.60 g of NS8 salt and 0.10 g of polyvinylpyrrolidone (PVP) were added and dissolved in 20 mL of ethylene glycol. The mixture was degassed in vacuum and polymerized at 130 °C for 8 h in a nitrogen stream with magnetic stirring at 600 rpm. The resulting polymer particles were purified by centrifugation of 10000 rpm for 20 min with water for three times.

2.4. Solid-State Polycondensation of salt monomer

Into a test tube, 0.50 g of NS8 salt was added and heated at 180 °C for 3 h under reduced pressure. The resultant polymer was washed with water and dried for 3 h under reduced pressure. Since endothermic peak temperature of NS8 salt was 274 °C [8], the polycondensation proceeded in solid state.

3. RESULTS AND DISCUSSION

3.1. Preparation of PI8 particles

3.1.1. Polycondensation of salt monomer (NS8) in ethylene glycol

Polycondensation of salt monomer derived from 1,8-diaminooctane (NS8) was performed in ethylene glycol at 130 °C in the presence of PVP as a steric stabilizer. The time-yield curve of polycondensation is shown in Figure 1. Before the

polycondensation, the solution was homogeneous. As the polycondensation proceeded, the solution was getting turbid after 1.5 h and the yield reached 96 % after 8 h. The electron micrographs of particles formed at various polycondensation times are shown in Figure 2. Particles with 4-12 μm diameters were formed as crystal nuclei by heating for 2 h. As the reaction proceeded, particles grew gradually. After 8 h, flower-like particles were formed and their diameters reached about 15 μm . Further polycondensation broke the particles into small pieces. Polycondensations were usually conducted with magnetic stirring at 600 rpm. Although stirring rate decreased from 600 rpm to 300 rpm, particles were still broken by the polycondensation for 24 h. Inherent viscosities of polyimides were slightly increased with polycondensation time, i.e., 0.07 dL/g for 1.75 h, 0.19 dL/g for 8 h, 0.23 dL/g for 24 h, and 0.27 dL/g for 120 h. Since most of monomer consumed after 8 h, further chain extension still proceeded and made shrinkage stress in the particles. Consequently particles might be broken to reduce the stress. We also tried to prepare particles for 24 h without stirring, different morphology with around 20 μm diameter was yielded. However many particles with 2-3 μm diameter were also formed.

Polycondensation of NS8 at different temperatures, 110°C or 150°C was conducted for 8 h. However, the polycondensation solution was not turbid at 110°C. Although PI particles were obtained quantitatively at 150°C, many small broken particles were obtained as prepared by the polycondensation at 130°C for 24 h. PVP was added into polycondensation system as a steric stabilizer. In the absence of PVP, the polycondensation of the salt monomer for 8 h afforded similar shaped particles with diameters ranging from 5 to 25 μm . Thus, the polycondensation using PVP made the particles with narrower size distribution (13-22 μm). Some polar solvents having high

boiling points were used in the polycondensation. Particles were not formed in *N,N*-dimethylacetamide or 1-methyl-2-pyrrolidinone, because of insolubility of the salt monomer. While, using protic solvents, such as 1,2-propanediol, 1,3-propanediol, and diethylene glycol, flower-like particles were also yielded by the polycondensation of the salt monomer. From an economical reason, ethylene glycol was used in the other polycondensations.

3.1.2. Characterization of PI8 Particles

The characteristic IR absorptions of the salt monomer were shown in 1500-1650 cm^{-1} ($-\text{N}^+\text{H}_3$) and 1733 cm^{-1} (ester). After polymerization, these peaks disappeared and the characteristic absorptions of imide rings appeared in 1771, 1746, and 729 cm^{-1} . In addition, there were no absorption bands of carboxylic acid and amide of the considerable intermediates, showing that the imidization proceeded quantitatively. The thermogravimetric analyses of polymers are shown in Figure 3. The temperature of degradation of polyimide without PVP was about 440 °C, while the weight of PI particles using PVP started to decrease at 380 °C, which was identical with the onset degradation temperature of PVP. Although the particles were purified by centrifugation with water three times, PVP was not completely removed from the particles.

3.2. Preparation of PIX particles

The polycondensations of salt monomers with diethyl pyromellitate and aliphatic diamine with various methylene lengths were conducted at 130 °C for 8 h or 24 h. The results are summarized in Table 1 and SEM images of particles prepared with 8 h are

shown in Figure 4. In most cases, the yields did not reach 100 % for 8 h. Although polymer yields reached around 100 % after 24 h, small pieces of particles were formed. Yields of some particles exceeded 100 %, which might be due to incorporation of PVP into PI particles as stated in 3. 1. 2. The inherent viscosities of polyimide prepared for 24 h were higher than those for 8 h. The polyimides prepared for 24 h with diamine (X= 6, 7, 9, 10, 11, and 12) had relatively high inherent viscosities and showed odd-even effect of methylene length. The inherent viscosity of polyimide with 1,11-undecanediamine reached 1.64 dL/g. Thus polycondensation reaction proceeded quantitatively at 130 °C for 24 h and the low inherent viscosity (X = 4, 5, 8, and 12) might be due to higher crystallinity of polymer. The polyimide was also afforded by solid-state polycondensation at 180 °C for 3 h (Table 1). The inherent viscosities of polyimide prepared with solid-state polycondensation were higher than those with solution polycondensation and showed clear odd-even effect of methylene length. The polyimides with odd-methylene length had high inherent viscosities. In the solid polymerization, all amino groups existed near ester and carboxylic acid because of ionic attraction, which made the polycondensation proceed smoothly. In the solution polymerization most of amino groups on the chain ends in the particle were not located near the ester and carboxylic acid, because the polyimide oligomer precipitated to form particle. Hence the chain extension reaction did not proceed smoothly in the particles. The particle shapes were also dependent on the chain lengths of diamines (X). Besides using 1,11-diaminoundecane (X=11), flower-like particles were obtained using all salt monomers. Especially, the particles with even-methylene-length diamine were made with large crystals.

3.3. Crystallinity of PI Particles

The melting points of PIX prepared with solution, solid-state, and the reported high-pressure polycondensation [8] are summarized in Table 2. Although the polyimides prepared in ethylene glycol had the lowest melting points due to their low inherent viscosities and containing a small amount of PVP, they had still high melting points in the range of 290-370°C. The melting points exhibited a distinctive odd-even effect of methylene chains with the higher values for the polyimides with even-numbered methylene chain.

Wide-angle X-ray diffraction patterns of polyimide prepared with solution polymerization in ethylene glycol and solid-state polymerization are summarized in Figure 5. The spectra of particles were almost same as those of the polyimide with solid-state polymerization. Since polyimide prepared with solid-state polymerization was related to monomer crystallinity, they had better crystallinity than those prepared with solution polymerization. The aliphatic polypyromellitimides had symmetrical and flat ring structure, and oligomer prepared in ethylene glycol was slowly precipitated onto crystallized polyimide particles during polycondensation. Thus crystal structure of polyimides was obtained. A series of polyimides except PI8 exhibited large diffraction peaks at the small-angle side near 5-6° in 2 θ . PI8 prepared with solid-state polycondensation also showed the 5-6° diffraction peak, however, PI8 prepared in ethylene glycol did not. This peak was not exhibited in the pattern of PI8 obtained by high-pressure polycondensation [8]. Since the PI8 yielded in ethylene glycol and by high-pressure polycondensation had low inherent viscosities (0.19 dL/g and 0.39 dL/g [8], respectively), these polymers might have different crystal structure from the solid state polymerization.

3.4. Reuse of ethylene glycol

From an environmental point of view, it is desirable that a solvent was reusable in the polycondensation. This polycondensation system contained salt-monomer, PVP, and ethylene glycol. After removal of PI particle by centrifugation, the collected ethylene glycol might be reused for another polycondensation solvent. Since polycondensation using NS10 salt afforded flower-like PI particles with relatively high inherent viscosity, this salt was used as monomer for polycondensation using the reused solvent. The serum of polycondensation solution after centrifugation (ca. 9 mL), 0.60 g of NS10 salt, 0.05g of PVP, and 11 mL of additional ethylene glycol were added into a flask and heated at 130 °C for 8 h. The inherent viscosities of the 2nd (0.23 dL/g) and the 3rd PI particles (0.26 dL/g) were a little lower than that of the 1st one (0.39 dL/g). Since ethanol and water were produced during the polycondensation, the reused solvent was more hydrophilic and prepared polyimide was likely to precipitate. Thus polyimide with lower inherent viscosity might be formed using the reused solvent. Although the reused solvent was used, PI particles were obtained in almost same shapes (Figure 2(d), and (e)).

4. CONCLUSIONS

Polycondensations of nylon-salt-type monomers composed with diethyl pyromellitate and aliphatic diamines were conducted in ethylene glycol to form flower-like particles. Nucleation was occurred by polycondensation for 1.5 h and particles grew to around 15 μm for 8 h. The polyimide particles showed the distinctive odd-even effect of the methylene chain of diamine in their inherent viscosity and crystallinity. The polyimide

particles using diamine with even-methylene length had higher crystallinity and lower inherent viscosity than those using diamine with odd-methylene length. Further investigations using other aromatic tetracarboxylic diesters are currently under way in our laboratory.

NOTE

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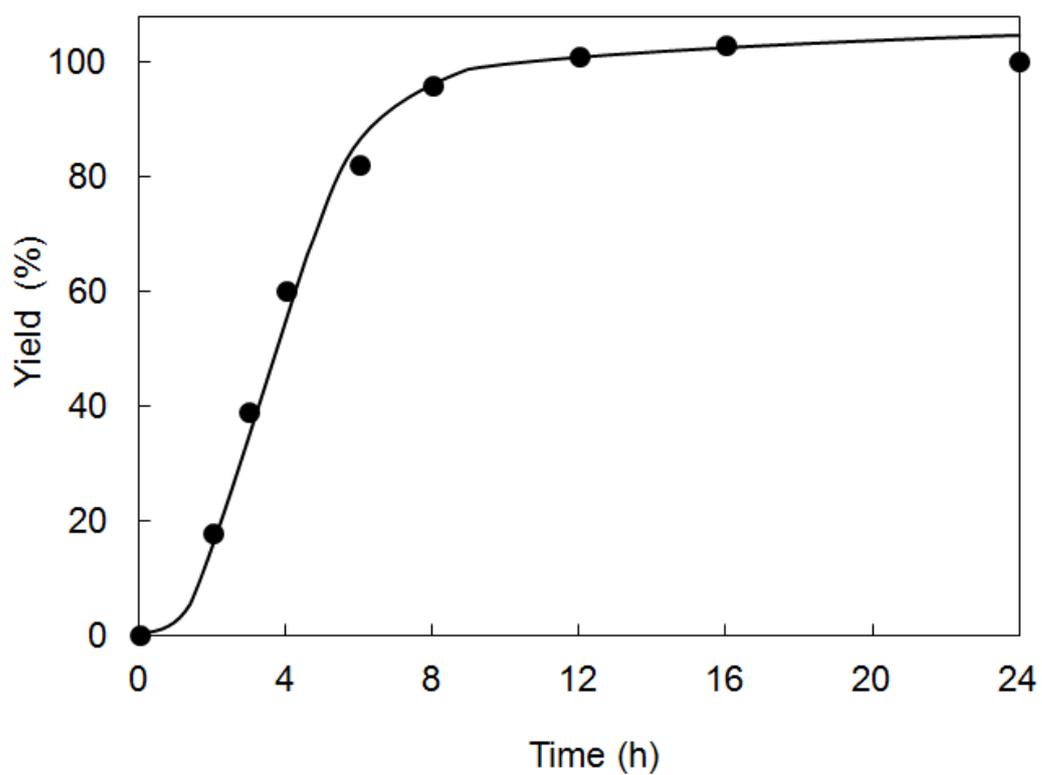


Figure 1. Time-yield curve of polycondensation of NS8 salt monomer at 130°C.

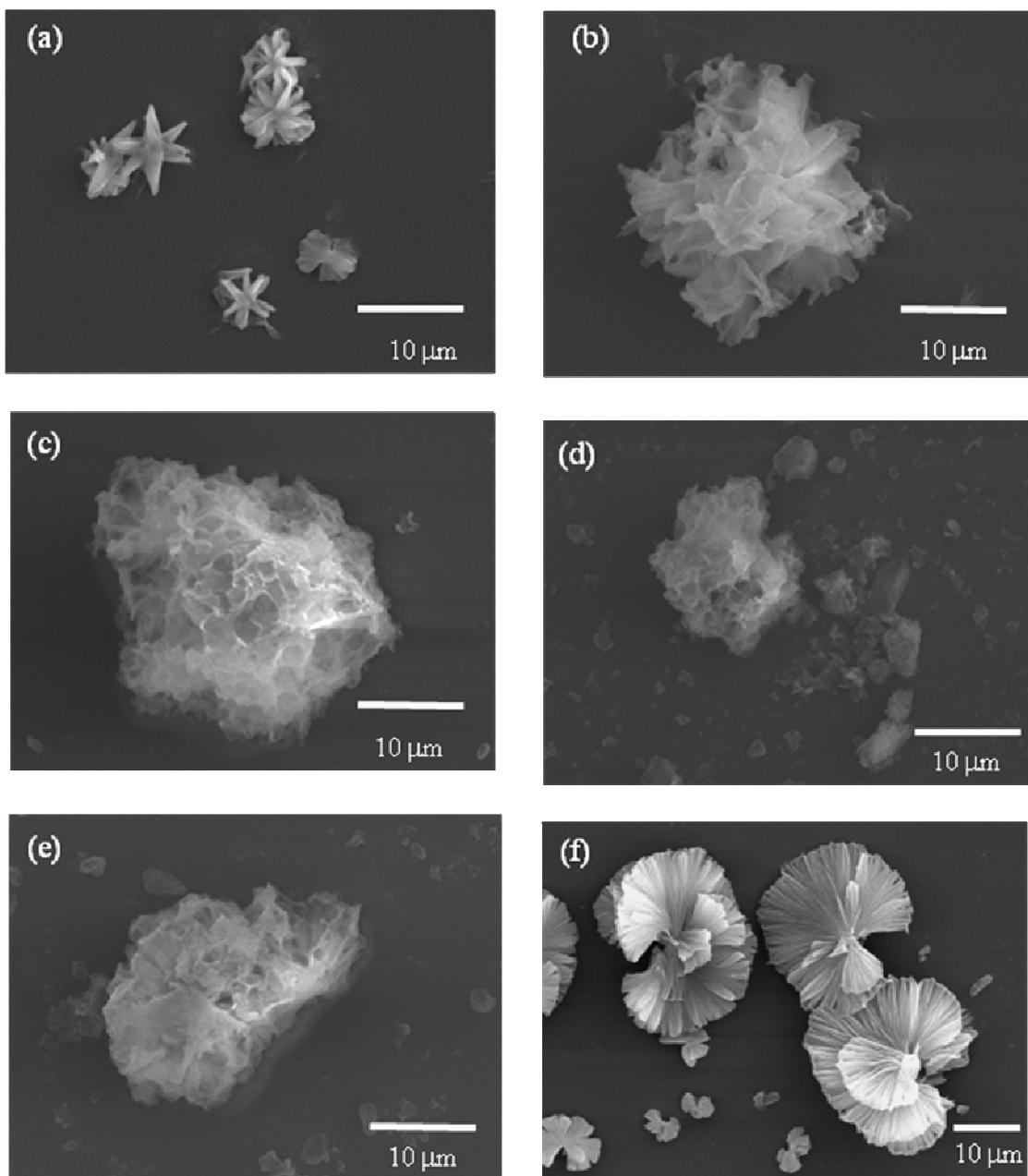


Figure 2. SEM images of PI8 particles prepared for (a) 2 h, (b) 3 h, (c) 8 h, (d) 16 h, (e) 24 h, and (f) 24 h without stirring.

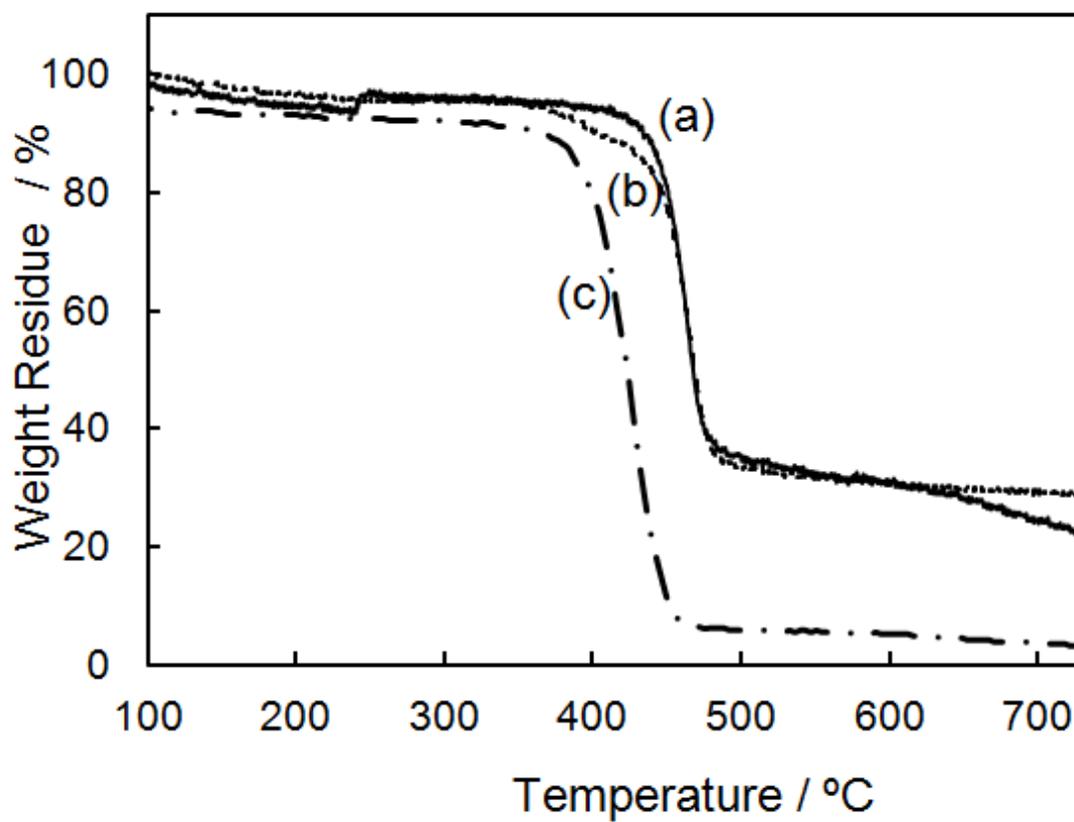


Figure 3. Thermogravimetric analysis (TGA) of (a) PI8, (b) PI8 particle, and (c) PVP. TGA was performed in argon atmosphere at a heating rate of 20 °C/min from room temperature to 750 °C.

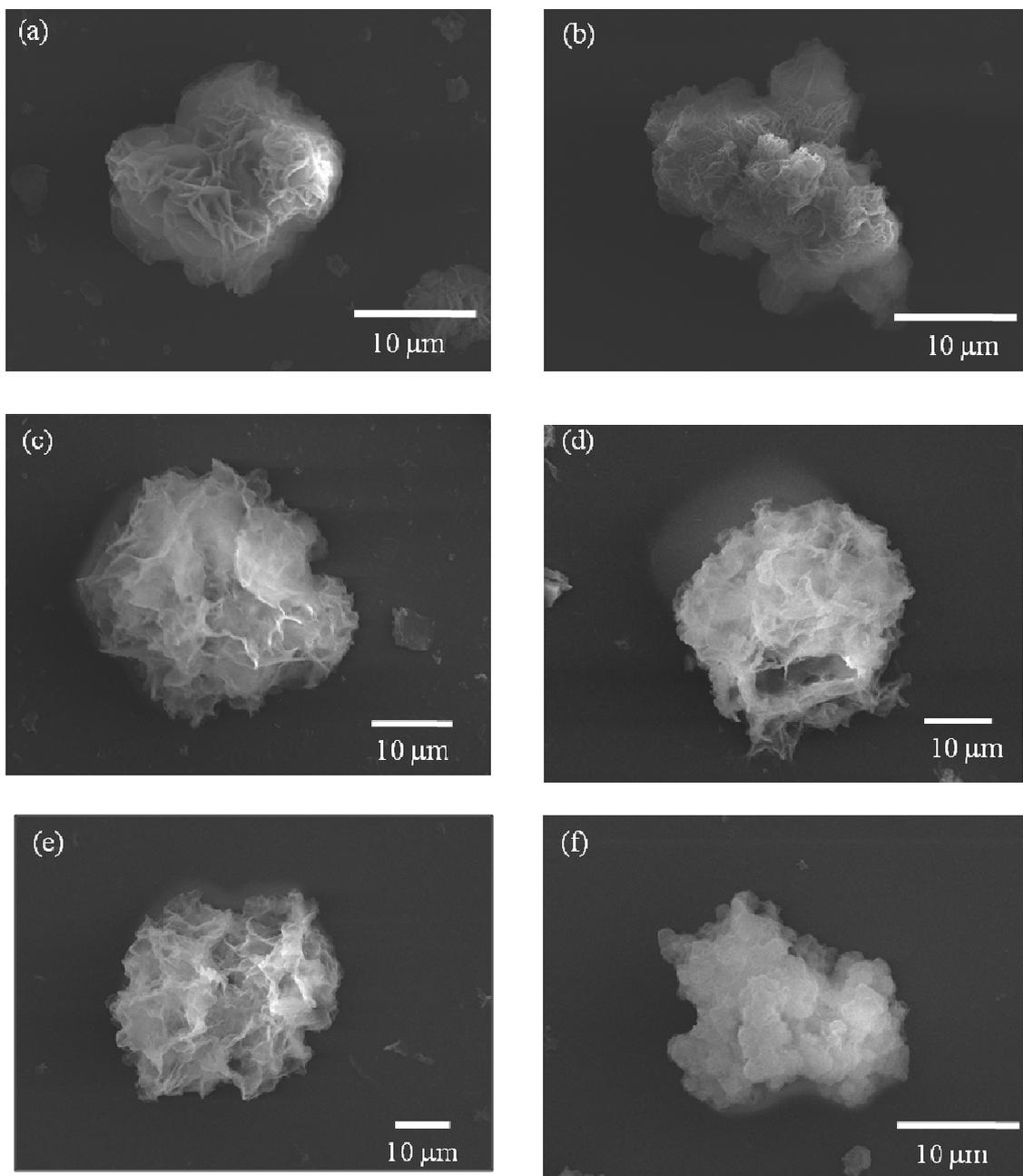
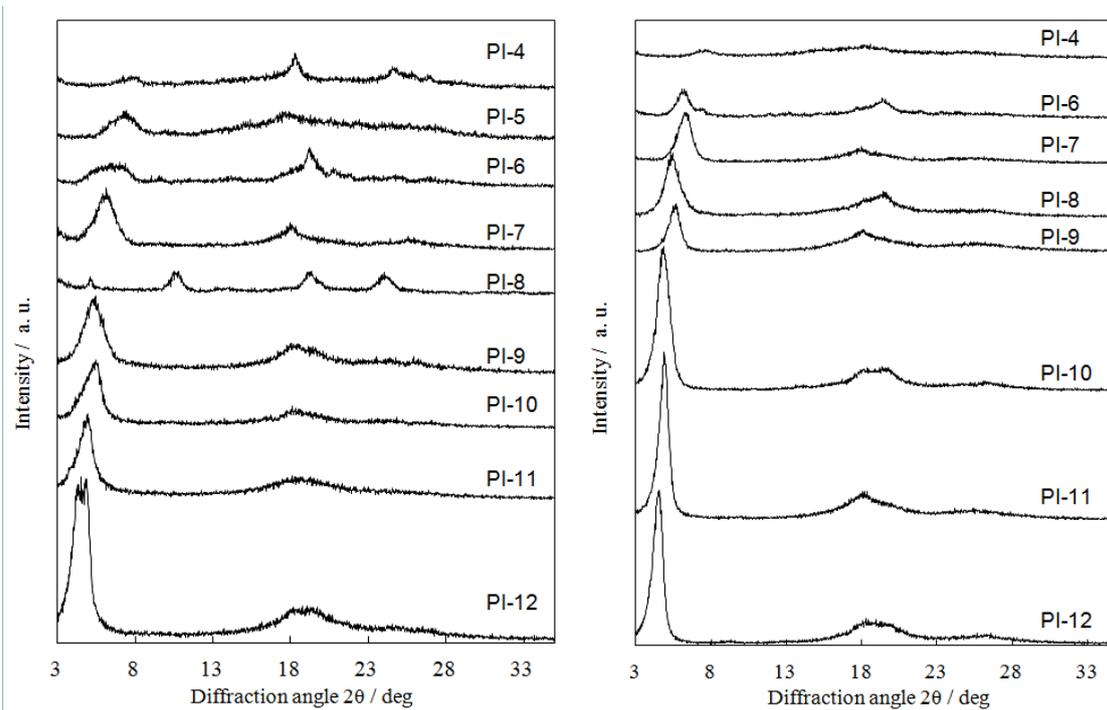


Figure 4. SEM images of PIX particles prepared for 8 h. (a) $X = 4$, (b) $X = 5$, (c) $X = 6$, (d) $X = 10$, (e) $X = 10$ (using reused solvent), and (f) $X = 11$.



(a)

(b)

Figure 5. Wide-angle X-ray diffraction of polyimides prepared with (a) solution polycondensation in ethylene glycol and (b) solid-state polymerization.

Table 1. Synthesis of PIX. ^a

Polyimide	<u>Yield (%)</u>		<u>Viscosity (dL/g)</u>			<u>Diameter (μm)</u>	
	<i>8 h</i>	<i>24 h</i>	<i>8 h</i>	<i>24 h</i>	<i>solid-state</i> ^b	<i>8 h</i>	<i>24 h</i>
PI4	100	104	0.17	0.22	0.46	9-26	7-20
PI5	93	96	0.21	0.30	1.04	8-23	13-40
PI6	83	105	0.29	0.53	0.93	4-35	10-46
PI7	92	104	0.26	0.49	1.42	7-41	11-35
PI8	100	105	0.19	0.23	0.70	13-22	11-25
PI9	83	101	0.29	0.63	1.51	9-26	20-40
PI10	97	104	0.31	0.53	0.93	8-63	8-100
PI11	79	103	0.31	1.64	1.18	7-46	7-30
PI12	88	105	0.29	0.44	0.66	24-61	8-79

^a NSX 0.60 g, PVP 0.10 g, and ethylene glycol 20 mL. Polycondensation was carried out at 130 °C.

^b Solid-state polycondensation was carried out at 180 °C for 3 h under reduced pressure.

Table 2. Melting points of PIX.

Polyimide	<i>solution</i> ^a	<i>solid-state</i> ^a	<i>high-pressure</i> ^b
PI7	333	346	348
PI8	368	379	374
PI9	302	314	318
PI10	311	336	347
PI11	289	289	299
PI12	291	309	321

^a Determined by DSC at a heating rate of 10°C min⁻¹ in argon atmosphere.

^b Ref.8.

Table 3. Synthesis of PI10 particles using reused solvent. ^a

<i>Step</i>	<i>Yield (%)</i>	<i>Viscosity (dL/g)</i>	<i>Diameter (μm)</i>
1 st	101	0.39	15-125
2 nd	90	0.23	16-105
3 rd	104	0.26	7-105

^a NS10 0.60 g, PVP 0.10 g, and ethylene glycol 20 mL. Polycondensation was carried out at 130 °C for 8 h.

