



# Preparation of monodisperse fully aromatic polyimide particles via the polycondensation of diethyl hexafluoroisopropylidenediphthalate with 4,4'-diaminodiphenylether in ethylene glycol

Shinji Watanabe<sup>1</sup> · Kozue Okamoto<sup>1</sup> · Takeshi Namikoshi<sup>1</sup> · Yoshihito Kohari<sup>1</sup> · Miki Murata<sup>1</sup>

Received: 2 August 2018 / Revised: 27 September 2018 / Accepted: 1 November 2018 / Published online: 3 December 2018  
© The Society of Polymer Science, Japan 2018

## Abstract

Fully aromatic polyimide particles were obtained in a single step via the polycondensation of diethyl (hexafluoroisopropylidene)diphthalate (6FE) and 4,4'-oxydianiline (ODA) using polyvinylpyrrolidone (PVP) as a steric stabilizer in ethylene glycol. Since the monomers are soluble in ethylene glycol, but the polyimide is insoluble, the polyimide particles grew gradually during the polycondensation process. The particle size and size distribution were controlled by varying the molecular weight and amounts of PVP. The particle size decreased with both increasing concentration and increasing molecular weight of the stabilizer. Furthermore, the solvent composition affected the particle size, i.e., the particle size decreased with increasing volume of glycerol as a cosolvent. Monodisperse particles (diameter: 8.5–1.8  $\mu\text{m}$ ) were obtained by varying the amounts of PVP and glycerol.

## Introduction

Dispersion polymerization is an effective method for the preparation of micron-sized monodisperse polymer particles in a single step [1–3]. The monomer is miscible in the reaction medium of the polymerization, but the resulting polymer is immiscible. In the beginning of polymerization, the solution, which contains monomer, steric stabilizer, and initiator, is homogeneous. As the polymerization proceeds, the prepared polymer forms nuclei, and the polymerization occurs in the particles and in the continuous phase. The polymerizations of styrene and (meth)acrylate were widely studied with regard to their kinetics and methods for controlling the size and size distribution in the 1990s. In general, the steric stabilizer and solvent composition influence the particle size and size distribution. Many steric stabilizers, such as polyvinylpyrrolidone, hydroxyl propyl cellulose, polyacrylic acid, and polymerizable macromonomers, have been employed in the dispersion polymerizations of styrene and (meth)acrylate using an aqueous

alcohol as the solvent. Using a suitable stabilizer and an appropriate medium, polymer particles 0.1–15  $\mu\text{m}$  in size with excellent monodispersity were obtained.

Fully aromatic polyimides (PIs) have been widely used in industrial applications, such as in aerospace, electronics, and gas separation membranes, owing to their excellent mechanical, thermal, and electronic properties. These materials are generally prepared through multistep processes, involving the ring-opening polyaddition of aromatic tetracarboxylic dianhydrides and aromatic diamines, which yields polyamic acids, and transformation to the polyimide is achieved through a thermal or a chemical treatment. Most aromatic PIs are insoluble in organic solvents and are intractable. Therefore, the commercial application of PIs is limited to coatings or films. The preparation of PI particles via solution polymerization [4, 5] and reprecipitation of a PI or polyamic acid solution into a poor solvent containing a polymeric stabilizer [6–8] has been attempted. Preparation of PI particles via dispersion polymerization has also been reported. The polymerization of benzophenonetetracarboxylic dianhydride with 4,4'-oxydianiline has been performed using polyvinylpyrrolidone as a steric stabilizer in a variety of organic solvents, i.e., methanol, acetone, ethyl acetate, and methyl acetate to afford polyamic acid particles. Further thermal treatment of the particles dispersed in xylene at 150 °C yielded PI particles with sizes ranging

✉ Shinji Watanabe  
watash@mail.kitami-it.ac.jp

<sup>1</sup> Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan

from 200 to 800 nm [9]. However, the size distribution of the particles was broad and two synthetic steps were necessary for preparing the PI particles.

In our group, semi aromatic PI particles were obtained via the polycondensation of an aromatic tetracarboxylic diethyl ester and an alkane diamine in ethylene glycol (EG), using polyvinylpyrrolidone (PVP) as a steric stabilizer [10, 11]. In contrast to the prepared polyimide, the resulting hydrophilic nylon salt monomers, were soluble in EG. The solution before polycondensation was homogeneous but became turbid after the start of the polycondensation due to the production of insoluble PI (nucleation). After nucleation, most of the polyimide generated in the solution had precipitated onto the particle surfaces as in the case of dispersion polymerization. Therefore, polyimide particles were formed via a single-step process using an appropriate steric stabilizer.

The particle shape was influenced by the monomer structure. Using diethyl pyromellitate and a diaminoalkane as monomers, flower-like particles were obtained due to the high crystallinity of the polyimide, and the size of the particles increased with increasing polymerization time [10]. Polycondensation using diethyl (hexafluoroisopropylidene)diphthalate (6FE) rather than diethyl pyromellitate yielded confetti-shaped particles [11]. The PI containing a flexible hexafluoroisopropylidene linkage is more soluble than the polypyromellitimide derivative and likely forms an amorphous solid, which yields particles that are morphologically different from the polypyromellitimide particles. Confetti-shaped particles have been obtained in several previous studies, but in most of cases, the particles were obtained through a multistep process. These processes included two-step polymerizations [12–14], heterocoagulation of different particles [15], dispersion polymerizations of styrene in the presence of methacrylate-coated SiO<sub>2</sub> particles [16], and the addition of water to a methanolic solution of poly(methyl methacrylate-co-vinylpyrrolidone) [17]. The one-step dispersion copolymerization of styrene with acrylonitrile by using a poly(ethylene glycol) macro-monomer also yields confetti-shaped particles [18]. The polycondensation of 6FE and an alkane diamine produced confetti-shaped particles in a single step with commercially available reagents [11].

In previous studies, although the size and shape of particles could be controlled to a certain degree, PI particles with a narrow size distribution were elusive [10, 11]. In this work, we prepared fully aromatic polyimide particles via the polycondensation of 6FE with 4,4'-oxydianiline (ODA). The fully aromatic PI was thermally and mechanically more stable than semiaromatic PI. Owing to the rigid main chain, the solubility of the fully aromatic PI in organic solvents was generally

very low, which might lead to difficulties in controlling the particle shape and particle distribution. Therefore, we employed 6FE, which has a flexible linkage between the benzene rings, as a monomer to increase the solubility of the PI oligomer, and we found that monodisperse PI particles could be obtained under the appropriate conditions. Controlling the particle size, size distribution, and shape was investigated by varying the PVP concentration and solvent composition.

## Experimental procedure

### Measurements

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6510A scanning microscope. The molecular weight and molecular weight distribution were measured at 40 °C via size exclusion chromatography (SEC) using a TOSOH HLC 8020 instrument equipped with a refractive index detector. *N,N*-dimethylformamide was used as the carrier solvent, and standard polyoxyethylenes were used for calibration. Fourier transform infrared (FT-IR) and <sup>1</sup>H NMR spectra were recorded using a JASCO FT/IR-660Plus and a JEOL nuclear magnetic resonance spectrometer (JNM-ECA600), respectively.

### Materials

Diethyl (hexafluoroisopropylidene)diphthalate (6FE) was prepared in accordance with a previously reported method [11]. 4,4'-Oxydianiline (ODA) and ethylene glycol (EG) were purified via sublimation and distillation from calcium hydride under reduced pressure, respectively. Other reagents were purchased from commercial supplier and were used as received.

### Polycondensation

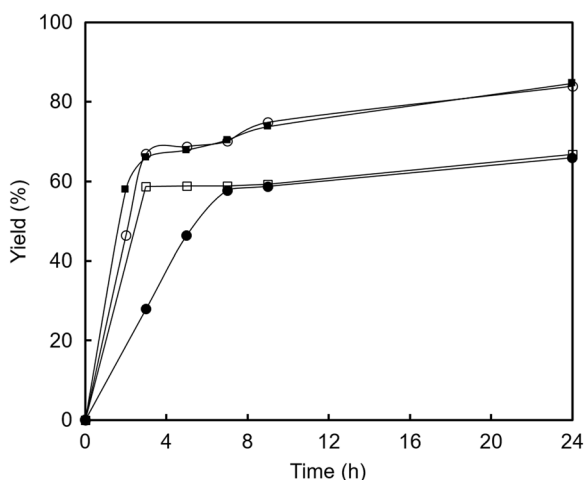
Into a 50-mL flask equipped with a condenser, 0.874 g (1.63 mmol) of 6FE, 0.326 g (1.63 mmol) of ODA, 0.20 g of polyvinylpyrrolidone (K-30), and 20 mL of EG were added. The solution was deoxygenated under vacuum and stirred for approximately 30 min at 90 °C until the monomers dissolved completely. The polycondensation was performed at 197 °C for 24 h with magnetic stirring at 800 rpm under a nitrogen atmosphere. The obtained particles were centrifuged at 10,000 rpm for 20 min with methanol and water (twice) and then lyophilized resulting in a yield of 85%. The prepared particles had an inherent viscosity of 0.46 dL/g in *N,N*-dimethylacetamide at 30 °C.

**Table 1** Polycondensation of 6FE with ODA at various temperatures and monomer concentrations

Run no.	Temperature (°C)	[6FE] <sub>0</sub> (mM)	Yield (%)	Inherent viscosity <sup>a</sup> (dL/g)	Dn (μm)	Dw/Dn
1	160	40.8	30	0.11	2.08	1.40
2	180	40.8	63	0.38	2.79	1.15
3	197	20.4	60	0.17	1.71	1.22
4	197	40.8	67	0.41	3.16	1.10
5	197	81.6	80	0.46	4.86	1.02
6	197	122	86	0.49	4.75	1.02

[6FE]<sub>0</sub> = [ODA]<sub>0</sub>, PVP(K 30) / 6FE = 1 / 4.37 (w/w), EG = 20 mL. Polycondensation was performed for 24 h

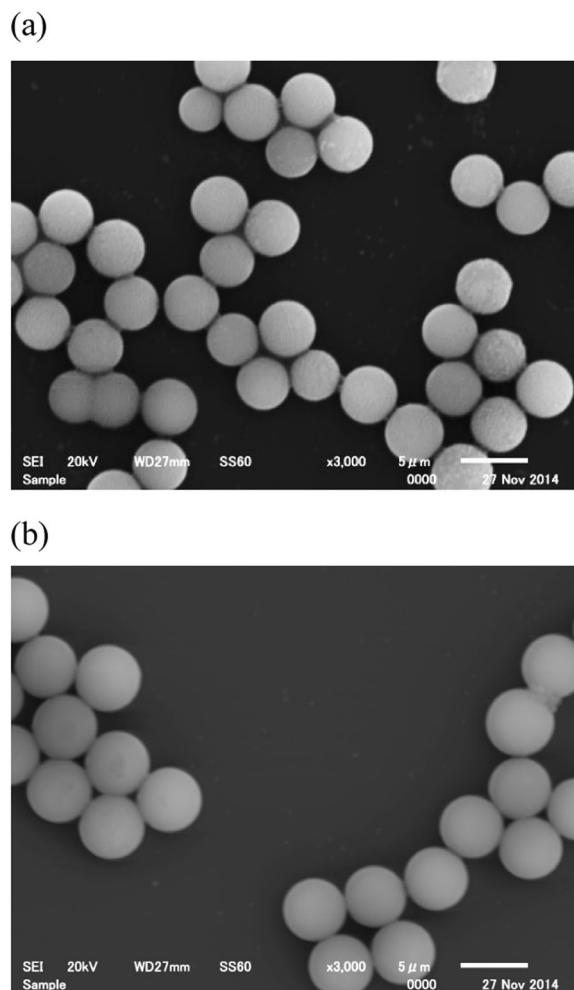
<sup>a</sup>Measured at a concentration of 0.5 g/dL in *N,N*-dimethylacetamide at 30 °C



**Fig. 1** Time-yield curves of 6FE polycondensations with ODA. PVP/6FE = 1/4.37 (w/w), EG = 20 mL, [6FE]<sub>0</sub> = [ODA]<sub>0</sub>; ●: [6FE]<sub>0</sub> = 40.8 mM at 180 °C, □: [6FE]<sub>0</sub> = 40.8 mM at 197 °C, ○: [6FE]<sub>0</sub> = 81.6 mM at 180 °C, and ■: [6FE]<sub>0</sub> = 81.6 mM at 197 °C

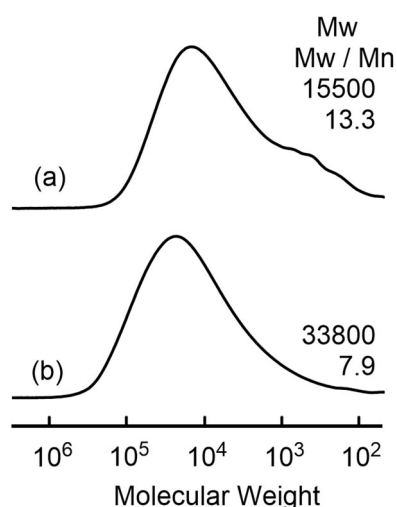
## Results and discussion

The polycondensations of 6FE and ODA were conducted using PVP as a steric stabilizer in EG to prepare polyimide (PI) particles in a single step. In a previous work, the polycondensation of 6FE and 1,8-diaminooctane was conducted at 130 °C [11]. Since ODA is less reactive than 1,8-diaminooctane, these polycondensations were conducted at 160–197 °C. The results are summarized in Table 1. At 160 °C, the yield and inherent viscosity of PI were both low (run no. 1). At 180 °C and 197 °C, polyimides with moderate inherent viscosities were obtained in ~60% yields (run nos. 2 and 4). The time-yield curves obtained for different polycondensation temperatures and monomer concentrations are shown in Fig. 1. The concentration of monomer [6FE]<sub>0</sub> has a significant effect on the yield. At [6FE]<sub>0</sub> = 81.6 mM, the yields of PI were 67% in 4 h and more than 80% after 24 h at both 180 and 197 °C, while only 67% yield of PI was achieved at [6FE]<sub>0</sub> = 40.8 mM in 24 h. The SEM micrographs of the PI particles obtained at [6FE]<sub>0</sub> = 81.6 mM after varying polymerization times are shown in



**Fig. 2** SEM micrographs of the PI particles prepared in 2 h (a) and in 24 h (b) at 197 °C. [6FE]<sub>0</sub> = 81.6 mM

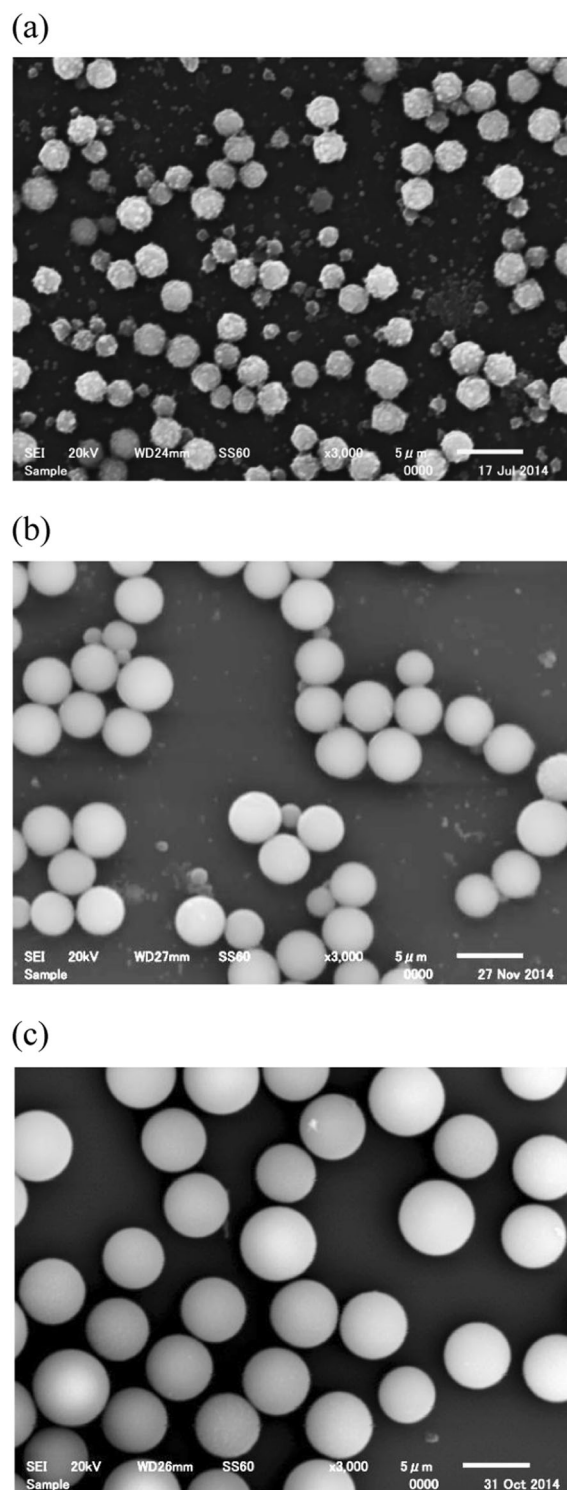
Fig. 2. Confetti-shaped particles were obtained with a polymerization time of 2 h (58% yield), while projection-free particles were formed in 24 h (85% yield). The corresponding SEC curves are shown in Fig. 3. For a polymerization time of 2 h, a broad peak corresponding to a relatively low molecular weight (peak molecular weight = 14700) and some small oligoimide peaks (molecular weight



**Fig. 3** SEC chromatograms of the PI particles prepared at 197°C in 2 h (a) and in 24 h (b).  $[6FE]_0 = 81.6$  mM. *N,N*-dimethylformamide was used as the eluent, and the molecular weight was calibrated with polyoxyethylene standards

<1000) were observed. After 24 h, the peak molecular weight was shifted to 22,400, and the low molecular weight peaks had disappeared. The solubility of the PI decreased with increasing molecular weight of PI, and PI with a molecular weight larger than a critical value will precipitate to form particles. Without the chain extension reaction in the particles, the polydispersity of the PI (Mw/Mn) should be smaller than the value calculated (2.0) for a step-growth condensation mechanism in a homogeneous system. The SEC curves of PI prepared in 2 and 24 h revealed PI polydispersities, that were considerably larger than the calculated value (2.0), suggesting that the chain extension reaction occurred frequently in the particles. From the FT-IR spectrum of the PI particles prepared in 24 h, bands assigned to the imide ring appeared  $1778$ ,  $1713$ , and  $745$   $\text{cm}^{-1}$ , and amide absorption bands, which typically appear at  $1650$  and  $1680$   $\text{cm}^{-1}$ , were absent, indicating that the imide rings were formed in the reaction at 197 °C for 24 h.

Polycondensations with various monomer concentrations were performed at 197 °C for 24 h. The results are summarized in Table 1, and SEM micrographs of the PI particles are shown in Fig. 4. At low monomer concentrations, confetti-shaped particles were obtained, and the inherent viscosities were low (run nos. 3 and 4), while monodisperse spherical particles were obtained at high monomer concentrations (run nos. 5 and 6), and the particle size increased with increasing monomer concentration. A preparing monodisperse particles, requires that the nucleation should be complete at a low conversion. At a high monomer concentration, the polycondensation rate was high and the nucleation stage should be relatively short compared with the particle growth stage, leading to the formation of monodisperse particles. Furthermore, the monomer



**Fig. 4** SEM micrographs of the PI particles: Run No. 3 (a), Run No. 4 (b), and Run No. 5 (c)

structure seemed to be important for the preparation of monodisperse particles. We tried to obtain poly-pyromellitimide particles that were more thermostable than the PI containing 6FE under the same polycondensation

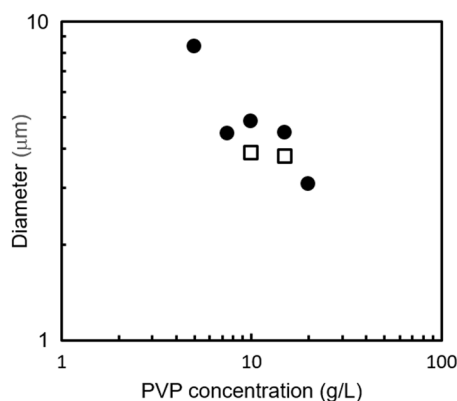


**Table 2** Preparation of PI particles using PVPs with different molecular weights

Run No.	PVP (g) <sup>a</sup>	Yield (%)	Dn (μm)	Dw/Dn	Shape
7	K 15: 0.200	62	7.43	1.09	Confetti
8	K 15: 0.300	70	4.26	1.46	Confetti
9	K 30: 0.050	64	8.59	1.47	Confetti
10	K 30: 0.100	73	8.36	1.02	Confetti
11	K 30: 0.150	81	4.45	1.01	Confetti
5	K 30: 0.200	80	4.86	1.02	Sphere
12	K 30: 0.300	85	4.46	1.02	Sphere
13	K 30: 0.400	86	3.09	1.06	Sphere
14	K 90: 0.200	80	3.86	1.01	Sphere
15	K 90: 0.300	84	3.78	1.03	Sphere

[6FE]<sub>0</sub> = [ODA]<sub>0</sub> = 81.6 mM, EG = 20 mL. Polycondensations were performed at 197 °C

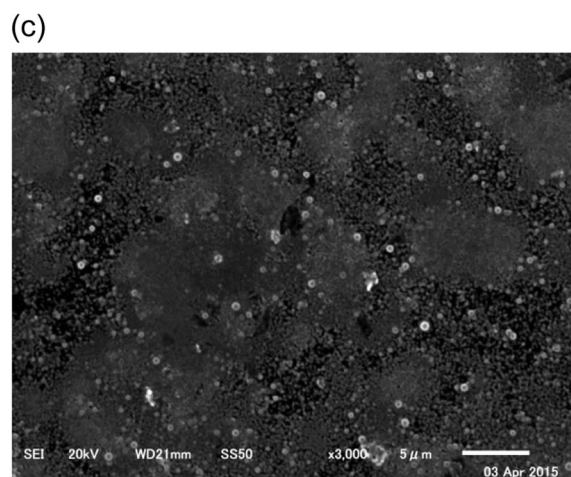
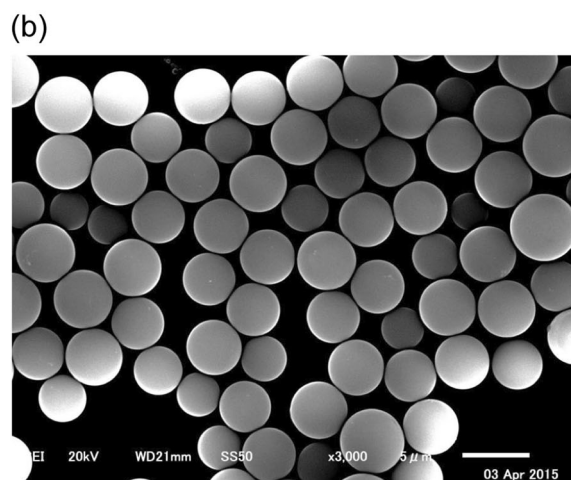
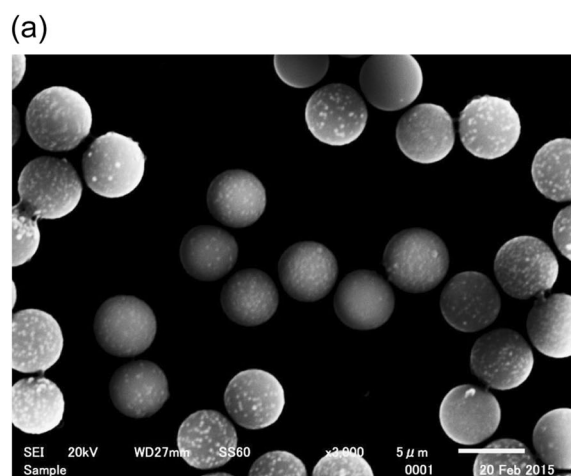
<sup>a</sup>K 15: molecular weight = 10,000, K 30: molecular weight = 40,000, K 90: molecular weight = 360,000



**Fig. 5** Effect of the PVP concentration on the particle size (●: K-30, □: K-90)

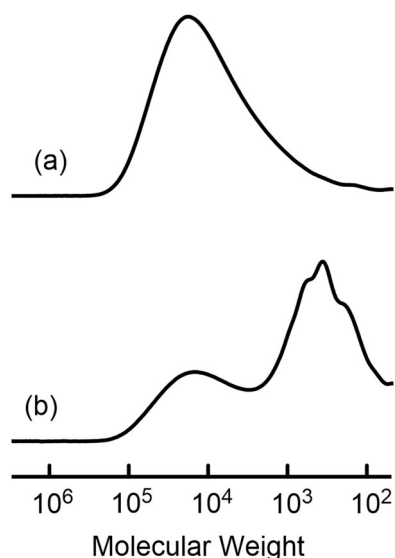
condition used in run no. 5 by replacing 6FE with diethyl pyromellitate. However, oddly shaped and flocculated particles were obtained. After nucleation, a growing PI chain in the medium accumulated around the particles. The polypyromellitimide chain was extremely rigid and insoluble in EG, which prevented the particle shape from changing, resulting in the formation of oddly shaped and colloiddally unstable particles. When 6FE with a flexible linker was used as the monomer, the accumulated PI chain on the particle could migrate to form a spherical particle in the particle growth stage.

In dispersion polymerization, the steric stabilizer has a crucial role in the stability of the particles. PVPs with different molecular weights, i.e., K-90 (molecular weight: 360,000), K-30 (molecular weight: 40,000), and K-15 (molecular weight: 10,000), were used in this polycondensation. The polycondensations are summarized in Table 2. The polycondensations using K-15 or a small amount of PVP yielded confetti-shaped particles with a



**Fig. 6** SEM micrographs of the PI particles (Run No.11) (a), collected via hot filtration (b), and secondary particles in the filtrate after hot filtration (c)

broad size distribution (run nos. 7–9). When K-30 or K-90 was used, small particles with a narrow size distribution were obtained. The effect of PVP on the resulting particle size is shown in Fig. 5. The particles prepared with K-90



**Fig. 7** SEC chromatograms of the PI particles (Run No. 11) collected via hot filtration (a), and secondary particles in the filtrate (b). *N,N*-Dimethylformamide was used as the eluent, and the molecular weight was calibrated with polyethylene oxide standards

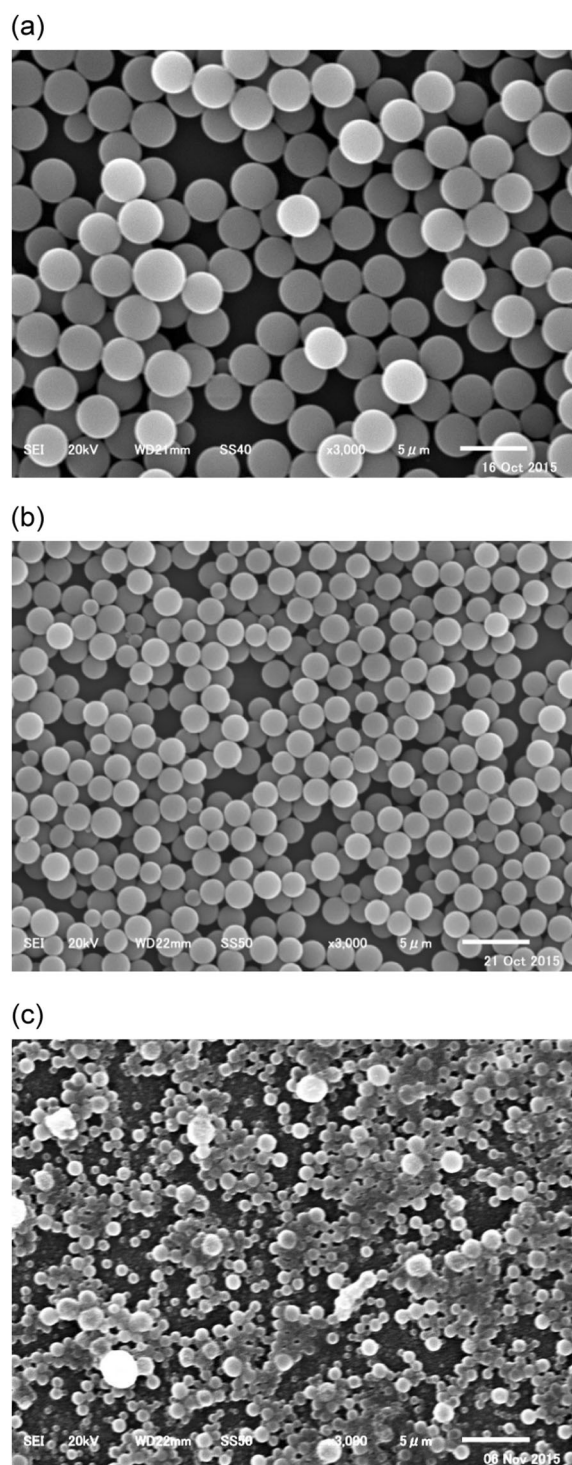
**Table 3** Preparation of PI particles in ethylene glycol / glycerol as the solvent

Run No.	Glycerol (mL)	Yield (%)	Dn ( $\mu\text{m}$ )	Dw/Dn
5	0	80	4.86	1.02
16	2	80	3.82	1.02
17	4	87	3.08	1.01
18	6	84	2.51	1.02
19	8	86	1.87	1.02
20	10	87	1.53	1.06
21	20	58	coagulation	

Total volume of solvent = 20 mL,  $[\text{6FE}]_0 = [\text{ODA}]_0 = 81.6 \text{ mM}$   
 PVP(K-30): 0.20 g. Polycondensation was performed at 197 °C

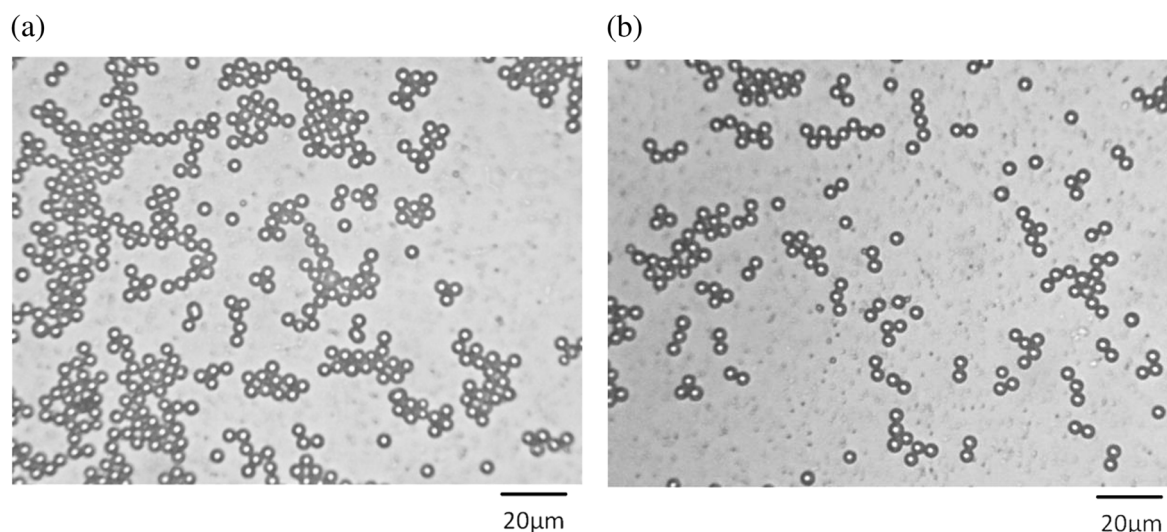
were slightly smaller than those prepared with K-30. As the figure shows, the particle size decreased from 8.4 to 4.5  $\mu\text{m}$  when the K-30 concentration was increased from 5.0 g/L to 15.0 g/L. The general effects of PVP on the particle size in the dispersion polymerizations of styrene [2, 19, 20], and MMA [21, 22] were that the particle size decreased with both increasing concentration and increasing molecular weight of the stabilizer. These results are consistent with the effects in the present polycondensation. High-molecular-weight PVP preferentially adsorbed onto the particle surface, leading to the formation of relatively small polymer particles.

The  $^1\text{H}$  NMR spectra of the PI particles show that the peaks derived from PVP, such as those at  $\delta$  3.2 and 2.1 ppm were absent, suggesting that most of the PVP was removed via centrifugation. In many free radical dispersion



**Fig. 8** SEM micrographs of the PI particles. Run No. 17 (a), Run No. 19 (b), and Run No. 21 (c)

polymerizations using PVP as a steric stabilizer, polymer was grafted onto the PVP chains via a radical transfer, leading to PVP adsorption onto the polymer particles and stabilization. In this polycondensation, PVP had a crucial effect on the particle size and



**Fig. 9** Optical micrographs of the PI particles (Run No. 5; see Table 2) before (a) and after (b) thermal treatment at 300 °C for 1 h

shape; however, it was not immobilized into the polyimide chain.

In our previous work, the polycondensation of 6FE with an alkane diamine also yielded confetti-shaped particles, and a mechanism for the formation of the particles was proposed. After the polycondensation, the polyimide oligomers in the medium precipitated by cooling to form small particles, which adsorbed onto larger particles to yield confetti-shaped particles [11]. Confetti-shaped particles were also formed in run no. 11, when the particle dispersion after polycondensation was cooled to room temperature (Fig. 6a). To remove the soluble PI oligomers from the larger particles, immediately after the polycondensation, the hot solution was filtered using a Buchner funnel (porosity 5–10 μm). Projection-free particles were obtained, and secondary particles (size < 0.8 μm) appeared in the filtrate, as shown in Fig. 6. The SEC curve of the particles collected via hot filtration was broad, and the peak molecular weight was ~20,000 (Fig. 7a). A large low-molecular-weight peak (< 2000) was obtained for the secondary particles (Fig. 7b). Therefore, the secondary particles were mainly derived from the soluble oligoimides at 197 °C, and these particles adsorbed onto the larger particles leading to confetti-shaped particles during the cooling of the solution. These particles were obtained after short polymerization times (Fig. 2a) or under low monomer concentrations (Fig. 4a). Under these conditions, an increased amount of oligoimide will remain in the medium, resulting in the formation of confetti-shaped particles after the polycondensation process.

The particle size is also affected by the solvent composition. The dispersion polymerization of styrene is often performed in a mixture of ethanol and water [19, 20], while the polymerization of methyl methacrylate is typically performed in a mixture of methanol and water to control the

particle size [21–24]. We selected ethylene glycol (relative permittivity:  $\epsilon_r = 38$ ) as a solvent for our system. Moreover, water ( $\epsilon_r = 78$ ) could not be used at 197 °C, and hence, glycerol ( $\epsilon_r = 43$ ) was used as the higher polarity solvent. Polycondensations with different volumes of glycerol were performed by keeping the total solvent volume fixed at 20 mL. The results of the dispersion polymerizations are summarized in Table 3, and SEM micrographs of the PI particles are shown in Fig. 8. Monodisperse particles were produced and the particle size decreased from 4.94 to 1.90 μm when the volume of glycerol was increased from 0 to 8 mL. The size distribution broadened with increasing glycerol (run no. 20), and the polycondensation with glycerol as the sole solvent yielded flocculated particles (run no. 21). With increasing glycerol, the critical chain length was shorter, and more nuclei were produced in the initial stage of the polymerization, resulting in a small particle size. Ethanol and water, the by-products of this polycondensation, may influence the particle size. However, in the  $[6FE]_0 = 81.6$  mM reaction, the produced ethanol and water only represented 0.27 wt% and 0.68 wt%, respectively, of the total medium and were generally absent from the medium, because the polycondensation was performed at 197 °C. Therefore, these products should have a negligible effect on the size and colloidal stability of the particles.

Optical micrographs of the PI particles before and after thermal treatment at 300 °C for 1 h are shown in Fig. 9. As the figure shows, the treatment has no effect on the particle shape because the glass transition temperature of this polyimide (i.e., 316 °C) is higher than the treatment temperature (300 °C) [25].

In conclusion, monodisperse polyimide particles with diameters ranging from 1.8 to 8.5 μm were prepared via the



polycondensation of 6FE and ODA using PVP as the steric stabilizer in an EG/GL solution. The particle diameter decreased with increasing amounts of PVP and GL. This method provides an easy access to monodisperse PI particles with high solid content suspensions. Studies focused on the functionalization of the PI and the usage of other monomers in the polycondensation are ongoing.

**Acknowledgements** This work was supported by JSPS KAKAENHI (Grant Number JP 16K05904) and performed under the Cooperative Research Program of the “Network Joint Research Center for Materials and Devices”.

## Compliance with ethical standards

**Conflict of interest** Notes The authors declare no competing financial interest.

## References

- Kawaguchi S, Ito K. Dispersion polymerization. *Adv Polym Sci*. 2005;175:299–328.
- Sudol, ED. Dispersion polymerization. *Polymeric dispersions: principles and applications* 141–54 (Springer, 1997).
- Ober CK. Dispersion copolymerization in non-aqueous media. *Makromol Chem Macromol Symp*. 1990;35/36:87–104.
- Wakabayashi K, Kohama S, Yamazaki S, Kimura K. Non-stoichiometric synthesis of poly(4,4'-oxydiphenylene pyromellitimide) by reaction-induced crystallization of oligomers. *Macromolecules*. 2008;41:1168–74.
- Wakabayashi K, Uchida T, Yamazaki S, Kimura K. Preparation of poly(4-phthalimide) nanoribbon by reaction-induced crystallization. *Macromolecules*. 2008;41:4607–14.
- Zhao G, Ishizaka T, Kasai H, Oikawa H, Nakanishi H. Fabrication of unique porous polyimide nanoparticles using a reprecipitation method. *Chem Mater*. 2007;19:1901–5.
- Zhao G, Ishizaka T, Kasai H, Hasegawa M, Nakanishi H, Oikawa H. Using a polyelectrolyte to fabricate porous polyimide nanoparticles with crater-like pores. *Polym Adv Technol*. 2009;20:43–47.
- Chai Z, Zheng X, Sun X. Preparation of polymer microspheres from solution. *J Polym Sci*. 2003;41:159–65.
- Ni X-W, Shen H, Chen L, Wu G, Lu R, Miyakoshi T. Synthesis of polyimide microparticles by dispersion polymerization. *J Appl Polym Sci*. 2009;113:3671–5.
- Watanabe S, Wakino A, Namikoshi T, Murata M. Preparation of aliphatic polypyromellitimide particles by polycondensation of nylon-salt-type monomers derived from aliphatic diamines with diethyl pyromellitate in ethylene glycol. *High Perform Polym*. 2012;24:710–6.
- Namikoshi T, Odahara K, Wakino A, Murata M, Watanabe S. Preparation of aliphatic–aromatic polyimide particles by polycondensation of diethylhexafluoroisopropylidenediphthalate and diaminoctane in ethylene glycol. *High Perform Polym*. 2015;27:183–90.
- Huang Y, Wang J, Zhou J, Xu L, Li Z, Zhang Y, et al. Controllable synthesis of latex particles with multicavity structures. *Macromolecules*. 2011;44:2404–9.
- Shi S, Zhou L, Wang T, Bian L, Tang Y, Kuroda S. Preparation of raspberry-like poly(methyl methacrylate) particles by seeded dispersion polymerization. *J Appl Polym Sci*. 2011;120:501–8.
- Huang H, Liu H. Synthesis of the raspberry-like PS/PAN particles with anisotropic properties via seeded emulsion polymerization initiated by  $\gamma$ -ray radiation. *J Polym Sci*. 2010;48:5198–205.
- Taniguchi T, Obi S, Kamata Y, Kashiwakura T, Kasuya M, Ogawa T, et al. Preparation of organic/inorganic hybrid and hollow particles by catalytic deposition of silica onto core/shell heterocoagulates modified with poly[2-(N,N-dimethylamino)ethyl methacrylate]. *J Colloid Interface Sci*. 2012;368:107–14.
- Nguyen D, Duguet E, Bourgeat-Lami E, Ravaine S. An easy way to control the morphology of colloidal polymer-oxide supraparticles through seeded dispersion polymerization. *Langmuir*. 2010;26:6086–90.
- Aranaz I, Reinecke H, Elvira C, Gallardo A. Compositionally-tunable surface nanostructuring of microspheres obtained from a self-stabilizing copolymerization of methyl methacrylate and vinylpyrrolidone. *Polymer (Guildf)*. 2011;52:2991–7.
- Chen MQ, Kaneko T, Akashi M. Preparation of “confetti” particles by dispersion copolymerization of acrylonitrile/styrene with poly(ethylene glycol) macromonomer. *Chem Lett*. 2001;30:1306–7.
- Bamnlolker H, Margel S. Dispersion polymerization of styrene in polar solvents: effect of reaction parameters on microsphere surface composition and surface properties, size and size distribution, and molecular weight. *J Polym Sci Part A*. 1996;14:1857–71.
- Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW. Uniform polymer particles by dispersion polymerization in alcohol. *J Polym Sci Part A*. 1986;24:2995–3007.
- Shen S, Sudol ED, El-Aasser MS. Control of particle size in dispersion polymerization of methyl methacrylate. *J Polym Sci Part A*. 1993;31:1393–402.
- Cao K, Yu J, Li B-G, Li B-F, Pan Z-R. Micron-size uniform poly(methyl methacrylate) particles by dispersion polymerization in polar media I. Particle size and particle size distribution. *Chem Eng J*. 2000;78:211–5.
- Kim OH, Lee K, Kim K, Lee BH, Choe S. Effect of PVA in dispersion polymerization of MMA. *Polymer*. 2006;47:1953–9.
- Watanabe S, Kobayashi T, Sumitomo H, Murata M, Masuda Y. Preparation of monodisperse PMMA particles by dispersion polymerization of MMA using poly(styrene-co-methacrylic acid) copolymer as a steric stabilizer. *Polym Bull*. 2010;65:543–50.
- Xiao X, Kong D, Qiu X, Zhang W, Zhang F, Liu L, et al. Shape-memory polymers with adjustable high glass transition temperatures. *Macromolecules*. 2015;48:3582–9.