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Micro-flowers of poly(*p*-phenylene pyromelliteimide) crystals

Kanji Wakabayashi [a], Tetsuya Uchida [b], Shinichi Yamazaki [a], Kunio Kimura [a,*]

[a] *Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*
[b] *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*

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ABSTRACT

Morphology control of poly(*p*-phenylene pyromelliteimide) (PPPI) crystals was examined using reaction-induced crystallization of oligomers during solution polymerization of self-polymerizable *N*-(4′-amino-phenyl)-3-carboxyl-4-alkoxycarbonylphthalimide. Micro-flowers of the PPPI needle-like crystals were formed in which the needle-like crystals grew radially from the center part as petals. The molecules aligned regularly along the long axis of the needle-like crystal. The structure of alkoxy group in the monomer and the monomer concentration influenced the size of the needle-like crystals, and their average length and width were changeable from 640 nm to 1.69 µm and from 110 nm to 210 nm, respectively. The average thickness was 20 nm. The obtained micro-flowers possessed high crystallinity and exhibited excellent thermal stability.

1. Introduction

Aromatic polyimides have been paid much attention as high performance polymers and they have been widely used [1–4]. Among them, poly(*p*-phenylene pyromelliteimide) (PPPI) is the most rigid polyimide, and therefore it is expectable to possess the highest performance [5,6]. Morphology of polymers with molecular orientation is of great importance to obtain essential properties, and the ideal morphology must be a one-dimensional structure such as a needle-like crystal and a fiber, especially for the usage as reinforcements. It is somewhat troublesome to control the morphology of PPPI with highly ordered molecular orientation by conventional techniques because of its intractability. In order to overcome the intractability, PPPI has been generally prepared by a two-step procedure *via* the synthesis of the corresponding soluble poly(amic acid) precursor, and the following imidization. However, the molecular orientation of poly(amic acid) precursor is difficult due to the structural irregularity caused by *meta* and *para* catenation of amide linkage, and the rapid crystallization during imidization prevents controlling the molecular orientation of PPPI [7,8]. Although various chemical modifications have been also attempted to improve its processability [7–11], these modifications usually decrease the essential properties predicted from the rigid molecular structure.

We studied the morphology control of PPPI using reaction-induced phase separation during isothermal polymerization of pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (PPDA) [12,13]. Lozenge-shaped crystals, aggregates of plate crystals and microspheres of PPPI were obtained so far. The previous results reveal that the behavior of the phase separation is significantly influenced by the degree of imidization of oligomer leading to the drastic change in the morphology of PPPI [12]. The structural irregularity of precursor oligo(amic acid) caused by *meta* and *para* catenation of amide linkage lowers the freezing point of the precipitated oligomers resulting in the induction of the liquid–liquid phase separation to form the microsphere. Further, the structural irregularity damages the crystallizability of the oligomers to form the crystals having clear habit. Additionally, the chemical structure of the oligomer end-groups also affects the morphology of the crystals [14,15]. In order to prepare the crystals having clear habit such as needle-like crystals by the crystallization of oligomers, it is at least necessary to precipitate the fully cyclized oligoimides having regular structure.

On the basis of these results, self-polymerizable monomers **1a** and **1b**, which contained an imide linkage, were designed as shown in Scheme 1 and the morphology control of PPPI was performed using reaction-induced crystallization during the polymerization of them.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA) was purchased from Aldrich Co. Ltd. and used as received. 4-Nitroaniline purchased from Tokyo Chemical Incorporation Co. Ltd. was used after recrystallization from acetone. Tetrahydrofuran (THF), *n*-hexane, methanol, ethanol and *N*-methyl-2-pyrolidone (NMP) were purchased from Nacalai Tesque Co. Ltd. THF and *n*-hexane were used after distillation over

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* Corresponding author. Tel./fax: +81 86 251 8902.
E-mail address: polykim@cc.okayama-u.ac.jp (K. Kimura).

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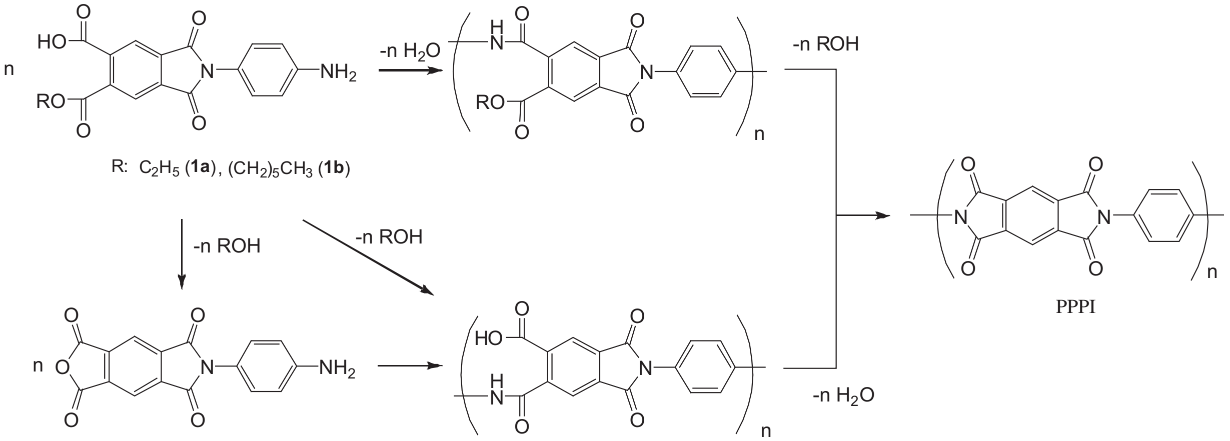


Scheme 1. Preparation of PPPI from self-condensation monomer; monomer **1** (R: $-C_2H_5$(**1a**), $-(CH_2)_5CH_3$)(**1b**)).

calcium hydride. Absolute methanol and ethanol were obtained by distillation over magnesium methoxide and magnesium ethoxide, respectively. NMP was used after dehydration over molecular sieves 4A. A mixture of isomers of dibenzyltoluene (DBT) was purchased from Matsumura Oil Co. Ltd. (Trade name: Barrel Therm 400, MW: 380, b.p.: 382 °C) and purified by distillation under reduced pressure (170–175 °C/0.2 mmHg).

2.2. *Measurements*

Morphology of the products was observed on a HITACHI S-3500N scanning electron microscope at 20 kV. Samples were dried, sputtered with platinum/palladium. Average shape parameters of the products were determined by taking the average of over 100 observation values. A selected-area electron diffraction (SAED) was taken by a JEOL 2000EX (Tokyo, Japan) transmission electron microscope (TEM) at 200 kV. ^{1}H NMR spectra were recorded on a JEOL AL300 SC-NMR at 300 MHz. Infrared (IR) spectra were recorded on a JASCO FT/IR-410 spectrometer. Wide angle X-ray scattering (WAXS) pattern was measured on a RIGAKU MiniFlex diffractometer with nickel-filtered CuKα radiation (35 kV, 20 mA). Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Daltonics AutoFLEX MALDI-TOF MS system operating with a 337-nm N_2 laser. Spectra were obtained in the linear positive mode with an accelerating potential of 20 kV. Mass calibration was performed with angiotensin I (MW 1296.69) and insulin B (MW 3496.96) from a Sequazyme peptide mass standard kit. The samples were then prepared by the evaporation–grinding method and measured in 3-aminoquinoline as a matrix doped with potassium trifluoroacetate salt according to the reported procedure [13,16]. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 with a scanning rate of 20 °C min^{-1} in N_2.

2.3. *Monomer synthesis*

2.3.1. *Pyromellitic monoanhydride (PMMA) (**2**)*

PMDA (43.6 g, 0.20 mol) and THF (400 mL) were placed into a three-necked round bottom flask equipped with a thermometer, a dropping funnel and a drying tube. THF solution (30 mL) contained water (5 mL, 0.28 mol) was added dropwise into the mixture at 20 °C over 48 h. After the addition, the solution was stirred for another 24 h. The solution was dried with sodium sulfate. 250 mL of THF was evaporated and absolute *n*-hexane was slowly added into the solution at 20 °C until precipitation occurred. The precipitates were removed by filtration and then filtrate was stood under −20 °C for 12 h. White needle crystals were collected by suction filtration and dried under vacuum at 40 °C for 12 h. The purity of PMMA **2** in the crystals was 96% estimated by ^{1}H NMR. Yield: 22 g (47%), m.p.: 273 °C. IR (KBr): 3100–2500, 1858, 1795, 1778, 1715, 1482, 1425, 1254, 1144, 1107, 1006, 890, 731, 683, ^{1}H NMR (300 MHz, acetone-d_6) δ(ppm): 8.38 (s, 2H).

2.3.2. *4,5-Dicarboxy N-(4′-nitrophenyl)phthalimide (CNPI) (**3**)*

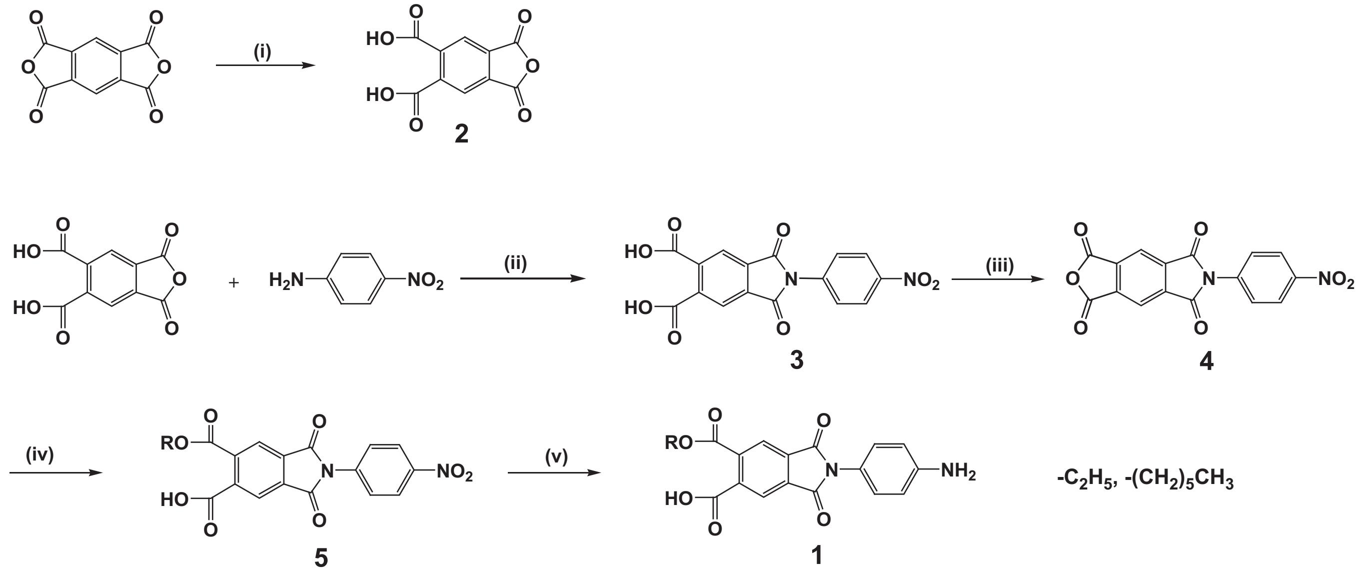
4-Nitroaniline (4.15 g, 0.03 mol) and NMP (50 mL) were placed into a three-necked flask equipped with a thermometer and a condenser. The solution was heated to 90 °C under N_2 atmosphere and then PMMA **2** (7.23 g, 0.03 mol) was added. The mixture was stirred for 30 min. The mixture was gradually colored to orange with time. Acetic anhydride (7 mL) and pyridine (0.5 ml) were added into the mixture at 100 °C and stirred for 3 h. After the filtration of the mixture, the filtrate was allowed to cool at 50 °C and then poured into 1 L of the water. The precipitates were collected by filtration and dried at 50 °C under vacuum for 12 h. Recrystallization from THF gave pale yellow crystals of CNPI **3** with yield of 52%. m.p.: 233 °C, IR (KBr, cm^{-1}): 3100–2500 (br), 1782, 1729, 1718, 1618, 1594, 1523, 1495, 1346, 1252, 1218, 1142, 1115, 1093, 1011, 928, 895, 845, 750, 695, ^{1}H NMR (300 MHz, acetone-d_6) δ(ppm): 8.46–8.43 (d, 2H, $J = 9.2$ Hz), 8.29 (s, 2H), 7.91–7.88 (d, 2H, $J = 9.2$ Hz). Anal. Calcd for $C_{16}H_8O_8N_2$ (356.24): C, 53.94; H, 2.26; N, 7.86. Found: C, 55.29; H, 3.54; N, 8.98.

2.3.3. *CNPI anhydride (**4**)*

CNPI **3** (3.5 g) and acetic anhydride (100 mL) were heated at 140 °C for 1 h in N_2 atmosphere. The reaction mixture was condensed by the distillation of acetic anhydride, and white solids were precipitated after cooling at 25 °C. The solids were collected by filtration and then recrystallized from acetic anhydride. CNPI anhydride **4** was obtained as white crystals with yield of 85%. m.p.: 272 °C. IR (KBr, cm^{-1}): 3109, 1866, 1778, 1726, 1596, 1525, 1516, 1459, 1375, 1348, 1299, 1206, 1120, 903, 839, 809, 746, 720, ^{1}H NMR (300 MHz, acetone-d_6) δ(ppm): 8.60 (s, 2H) 8.49–8.44 (m, 2H), 7.94–7.89 (m, 2H). Anal. Calcd for $C_{16}H_6O_7N_2$ (338.22): C, 56.78; H, 1.79; N, 8.28. Found: C, 60.81; H, 2.30; N, 6.28.

2.3.4. *4-Carboxy 5-ethoxycarbonyl N-(4′-nitrophenyl)phthalimide (CENPI) (**5a**)*

CNPI anhydride **4** (3.0 g) and ethanol (100 mL) were refluxed for 6 h. Ethanol was evaporated to obtain yellow solids. Recrystallization from ethanol gave white needle crystal of CENPI **5a** with yield of 81%. m.p.: 217 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ(ppm): 8.47–8.42 (m, 2H) 8.33 (d, 1H, $J = 0.5$ Hz), 8.22 (d, 1H, $J = 0.5$ Hz), 7.92–7.87 (m, 2H), 4.44–4.37 (q, 2H, $J = 7.2$ Hz), 1.39–1.35 (t, 3H, $J = 7.2$ Hz). IR (KBr, cm^{-1}): 3117, 3059, 2998, 3100–2500 (br), 1787,



Scheme 2. Synthesis of monomer **1** (R: $-C_2H_5$(**1a**), $-(CH_2)_5CH_3$(**1b**)) (i) H_2O, THF; (ii) (1) NMP, 100 °C, (2) Acetic anhydride/pyridine; (iii) Acetic anhydride, reflux; (iv) Ethanol or 1-hexanol, reflux; (v) H_2, ethanol or methanol. 25 °C.

1730, 1697, 1594, 1520, 1494, 1448, 1385, 1343, 1289, 1266, 1221, 1138, 1104, 849, 720. Anal. Calcd for $C_{18}H_{12}O_8N_2$ (384.30): C, 56.22; H, 4.16; N, 7.29. Found: C, 56.14; H, 2.91; N, 7.16.

2.3.5. *4-Carboxy 5-hexyloxycarbonyl N-(4′-nitrophenyl) phthalimide (CHNPI) (**5b**)*

CNPI anhydride **4** (4.5 g) and 1-hexanol (50 mL) were heated at 120 °C for 3 h. The mixture was allowed to cool at 25 °C. White leaf-like crystal was precipitated. Recrystallization from 1-hexanol gave white leaf-like crystals of CHNPI **5b** with yield of 3.6 g (62%). m.p.: 176 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ(ppm): 13.99 (s, 1H), 8.44–8.41 (d, 2H, $J = 9.0$ Hz), 8.23 (s, 1H), 8.19 (s, 1H), 7.81–7.79 (d, 2H, $J = 9.2$ Hz), 4.30–4.26 (t, 2H, $J = 6.6$ Hz), 1.74–1.65 (m, 2H), 1.39–1.29 (m, 6H), 0.89–0.84 (t, 3H, $J = 6.8$ Hz). IR (KBr, cm^{-1}): 3400–2400 (br), 2922, 2856, 1784, 1736, 1692, 1592, 1523, 1496, 1404, 1341, 1285, 1223, 1126, 1114, 1054, 858, 751, 720. Anal. Calcd for $C_{22}H_{20}O_8N_2$ (440.40): C, 60.00; H, 4.58; N, 6.36. Found: C, 59.09; H, 3.78; N, 7.46.

2.3.6. *N-(4′-Aminophenyl)-3-carboxyl-4-ethoxycarbonylphthalimide (**1a**)*

CENPI **5a** (1.5 g) and absolute ethanol (300 mL) were placed into a three-necked round bottom flask equipped with a thermometer and gas inlet and outlet tubes. 10% Pd/C (0.15 g) was added and the mixture was vigorously stirred under H_2 atmosphere at 25 °C for 6 h. Pd/C was removed by filtration with celite and the filtrate was evaporated at 25 °C. Recrystallization from the mixed solvent of methanol and water (v/v 5/1) gave pale yellow needle crystals of monomer **1a** with the yield of 39%. m.p.: 227–255 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ(ppm): 8.12 (s, 1H), 8.09 (s, 1H), 7.04–7.01 (d, 2H, $J = 8.4$ Hz), 6.65–6.62 (d, 2H, $J = 8.6$ Hz), 4.36–4.29 (q, 2H, $J = 7.0$ Hz), 1.33–1.28 (t, 3H, $J = 7.2$ Hz). IR (KBr): 3476, 3377, 2978, 2871, 2612, 2104, 1780, 1719, 1620, 1601, 1519, 1469, 1427, 1375, 1344, 1261, 1220, 1177, 1131, 738. Anal. Calcd for $C_{18}H_{14}O_6N_2$ (354.31): C, 61.00; H, 3.98; N, 7.91. Found: C, 60.10; H, 4.40; N, 6.31.

2.3.7. *N-(4′-Aminophenyl)-3-carboxyl-4-hexyloxycarbonylphthalimide (**1b**)*

Monomer **1b** was prepared from CENPI **5b** and methanol in the similar manner of monomer **1a**. Recrystallization from mixed solvent of methanol and water (v/v 5/1) below 50 °C afforded needle crystals of monomer **1b** with the yield of 44%. m.p.: 174 °C, ^{1}H NMR (300 MHz, DMSO-d_6) δ(ppm): 8.12 (s, 1H), 8.07 (s, 1H), 7.03–7.01 (d, 2H, $J = 8.6$ Hz), 6.65–6.62 (d, 2H, $J = 8.6$ Hz), 4.29–4.24 (t, 2H, $J = 6.4$ Hz), 1.73–1.64 (m, 2H, $J = 6.4$ Hz), 1.39–1.28 (m, 6H), 0.88–0.84 (t, 3H, $J = 6.4$ Hz). IR (KBr): 3483, 3388, 3051, 3002, 2932, 2605, 1780, 1727, 1719, 1621, 1602, 1580, 1518, 1469, 1428, 1372, 1264,

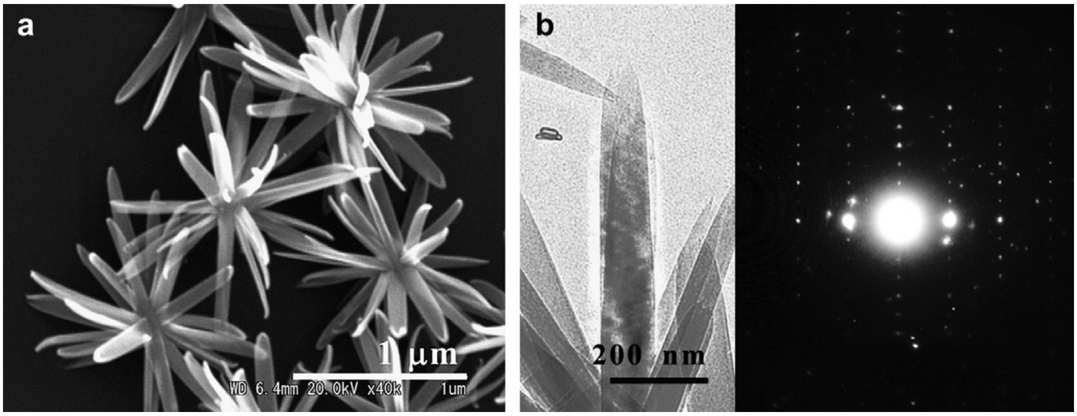


Fig. 1. (a) A SEM and (b) a TEM image with a selected-area electron diffraction pattern of the PPPI crystals prepared from monomer **1a** at a concentration of 0.25% (run no. 2).

1221, 1132, 1023, 1024, 784. Anal. Calcd for $C_{22}H_{22}O_6N_2$ (410.65): C, 64.82; H, 5.40; N, 6.82. Found: C, 64.28; H, 5.27; N, 6.73.

2.4. Polymer preparation

DBT (20 mL) was placed into a cylindrical flask equipped with gas inlet and outlet tubes, and heated up to 330 °C in N_2 atmosphere. Monomer **1a** (0.061 g, 0.17 mmol) was added into the solution at 330 °C under stirring. The stirring was stopped when monomer **1a** was entirely dissolved. The polymerization was carried out at 330 °C for 6 h with no stirring. Polymerization concentration, defined as (calculated polymer weight/solvent volume) X 100 in this study, was 0.25%. The solution became turbid immediately and the pale yellow crystals were formed with time. After 6 h, the crystals were collected by filtration at 330 °C to avoid the precipitation of oligomers during cooling. The collected crystals were washed with *n*-hexane and acetone several times, and then dried at 25 °C for 12 h. Oligomers dissolving in the solution at 330 °C were collected by pouring the filtrate into *n*-hexane. The precipitated oligomers were collected by filtration, washed with *n*-hexane and fried at 40 °C under vacuum for 12 h. Polymerizations of monomer **1b** were also carried out in a similar manner.

3. Results and discussion

Three polymerization routes are possibly thought as also depicted in Scheme 1, that is, *via* a direct amidation with elimination of water, *via* an amidation with elimination of alcohol, and *via* a formation of anhydride. The monomers were synthesized from the pyromellitic monoanhydride and *p*-nitroaniline as shown in Scheme 2. Polymerizations were carried out at 330 °C in a mixture of dibenzyltoluene isomers at a concentration of 0.15–0.5%. The solution was stirred until the monomers were entirely dissolved and then the polymerization was continued without stirring in N_2 atmosphere. The solution became turbid in the initial stage of the polymerization, and then the crystals grew with time. After 6 h, the crystals formed in the solution were collected by filtration. Table 1 presents results of the polymerizations.

Yields of the crystals were 67–82% and they increased with the concentration. Fine flowers comprised of needle-like crystals were formed under these conditions. The flower-like crystals obtained from monomer **1a** at a concentration of 0.25% were representatively shown in Fig. 1.

The needle-like crystals grew radially from the center part as petals. The average length, width and thickness of the needle-like crystals were 710, 110 and 20 nm, respectively. The width and the thickness did not change depending on the concentration, but the length slightly increased with the concentration. Chemical structure of the needle-like crystals was measured on FT-IR spectrometry.

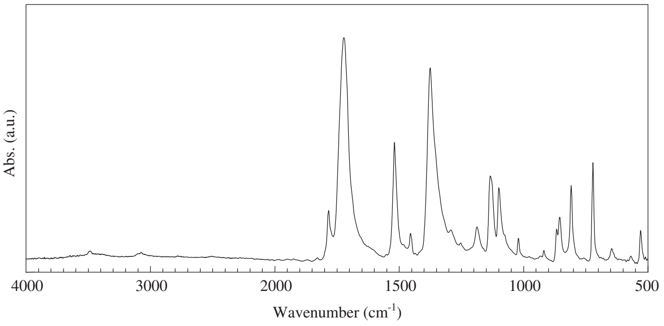


Fig. 2. IR absorption spectrum of PPPI crystals prepared from monomer **1a** at a concentration of 0.25% (run no. 2).

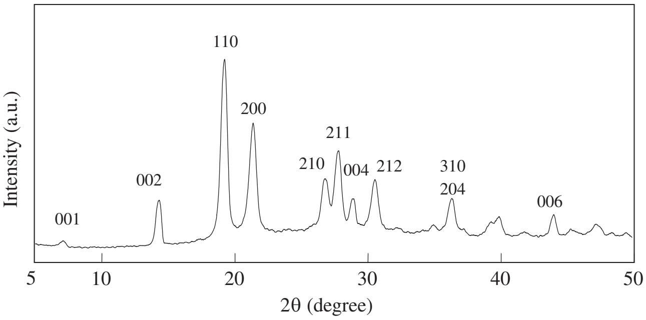


Fig. 3. WAXS intensity profile of PPPI crystals prepared from monomer **1a** at a concentration of 0.25% (run no. 2).

Fig. 2 is the spectrum of the needle-like crystals prepared at a concentration of 0.25% (run no. 2). Characteristic bands of C═O and C─N stretching of imide linkage clearly appeared at 1780, 1720 cm^{-1} and 1380 cm^{-1}, respectively. The bands of an amide linkage and a carboxylic acid were not observed at all. Furthermore, the bands of end-groups such as amino, an ethyl ester, a carboxyl and an anhydride group had disappeared. These results show that high molecular weight PPPI was prepared as a form of the needle-like crystal. In a WAXS intensity profile of the needle-like crystal, refraction peaks were very sharp and diffuse halo caused by an amorphous part could hardly be detected as shown in Fig. 3.

The needle-like crystals possessed quite high crystallinity. All peaks could be assigned by the orthorhombic unit cell of PPPI previously reported [5,17]. To examine the molecular alignment in the crystal, a selected-area electron diffraction was taken as shown in Fig. 1. A diffraction pattern was not a true fiber pattern of cylindrical symmetry and it was like a single crystal pattern. These diffractions could be also assigned according to the orthorhombic unit cell of PPPI and the *c* axis was identical with the direction of the long axis of the needle-like crystal. This result reveals that the PPPI molecules align regularly along the long axis of the crystal. This needle-like morphology with the molecular orientation is desirable to obtain the essential properties as aforesaid.

In order to clarify the structure of the precipitated oligomers, the oligomers recovered from the solution at the initial stage of the polymerization were analyzed by MALDI-TOF mass spectrometry. The spectrum and the peak assignments were shown in Fig. 4 and Table 2. A monomer and oligomers up to tetramers mainly composed

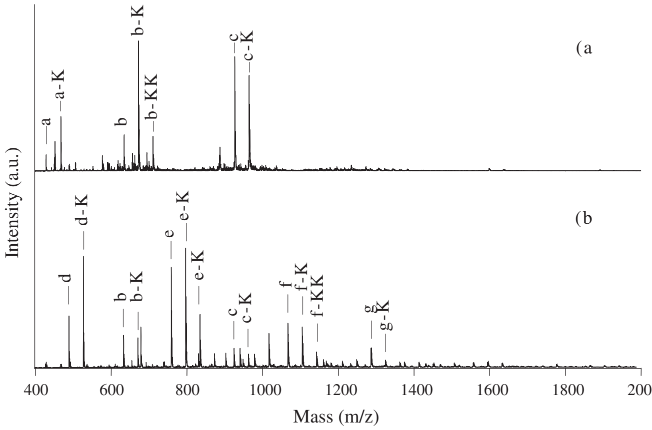


Fig. 4. MALDI-TOF mass spectra of oligomers recovered from solution after 10 min of polymerization of monomer **1a** at a concentration of 0.25%. (a) Dithranol and (b) 3-aminoquinoline were used as matrices. Peak code “a-K” means one potassium adduct of an oligomer assigned by peak code ‘a’ shown in Table 2.

Table 1
Preparation of PPPI crystals.[a]

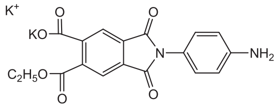
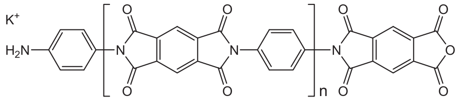
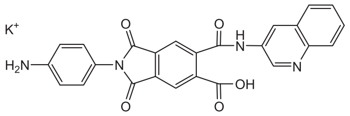
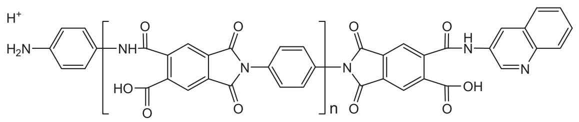
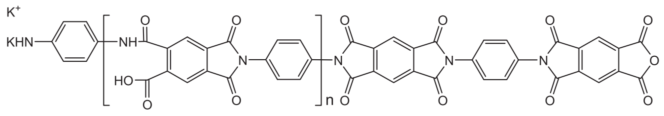
Run no.	Polymerization conditions		Yield (%)	Average size of needle-like crystals		T_{10}[c] (°C)
	Monomer	Conc. (%)		Length[b] (nm)	Width (nm)	
1	**1a**	0.15	66.7	640	110	674
2		0.25	73.0	710	110	610
3		0.50	81.6	720	110	598
4	**1b**	0.1	86.0	660	120	653
5		0.25	87.6	810	130	677
6		1.0	94.9	1230	150	687
7		2.0	97.5	1690	210	656

[a] Polymerizations were carried out in a mixture of dibenzyltoluene isomers at 330 °C for 6 h.
[b] Length of needle-like crystals from center part.
[c] Temperatures of 10 wt% loss were measured on a TGA with a heating rate of 20 °C min^{-1}.

of imide linkages were detected. The oligoimides larger than pentamers might be precipitated to form the needle-like crystal and the polymerization proceeds in the crystals to increase molecular weight. In this self-polymerization, both the structural regularity of oligoimide end-groups and the stoichiometric balance between two reactive end-groups are strictly compensated comparing with the polymerization of PMDA and PPDA. The drawbacks for the preparation of the crystals caused by the structural irregularity of oligo (amic acid) were completely conquered. The needle-like crystals, so-called whiskers, of aromatic polymers had been prepared by the crystallization during the isothermal polymerization [18,19]. The spiral growth mechanism caused by the screw dislocation had been proposed as one of the possible mechanisms of the whiskers. Based on the robust similarity of the morphological feature with the molecular alignment, it is likely thought that the PPPI needle-like crystals may be formed according to the mechanism similar to the whisker. As aforesaid, the needle-like crystals grew radially from the center part as petals. The nuclei for needle-like crystals might aggregate, bringing about the flower-like morphology. The formation mechanism of the PPPI needle-like crystal has not been clarified so far, and further study is needed.

Hexyl ester monomer **1b** was polymerized instead of ethyl ester monomer **1a** to investigate the influence of oligomer end-groups on the morphology. Results were also summarized in Table 1. The polymerization of monomer **1b** also afforded the PPPI needle-like crystals at a concentration of 0.15–2.0% with the yield of 86–98% as shown in Fig. 5. The sizes of the crystals prepared at a concentration of 0.1% were averagely 660 nm in length, 120 nm in width and 20 nm in thickness. Higher concentration gave longer the needle-like crystals. The sizes of the crystals prepared at a concentration of 2.0% were averagely 1.69 μm in length and 210 nm in width. The thickness was 20 nm. From the MALDI-TOF mass spectroscopy, the needle-like crystals from monomer **1b** were formed by the crystallization of fully cyclized oligoimides. Based on this fact, the cyclized oligoimides are precipitated to form the crystals, and hence, the morphology of the crystals is not so susceptible to the chemical structure of monomers. The width of the needle-like crystals prepared from monomer **1b** is larger than that from monomer **1a** at the same concentration. The size of the crystals is generally determined by both the size of nucleus, which relates to the degree of super-saturation, and the

Table 2
Structural assignments of peaks detected in MALDI-TOF mass spectra.

Peak code[a]	Mass (*m*/*z*)		Structure	*n*
	Obs.	Calc.		
a	428.78	430.52		
b	634.75	636.58		1
c	926.87	926.81		2
d	490.82	490.53		
e	761.06	761.68		1
f	1069.1	1069.9		2
g	1289.9	1069.9		2

[a] Peak codes were shown in Fig. 4.

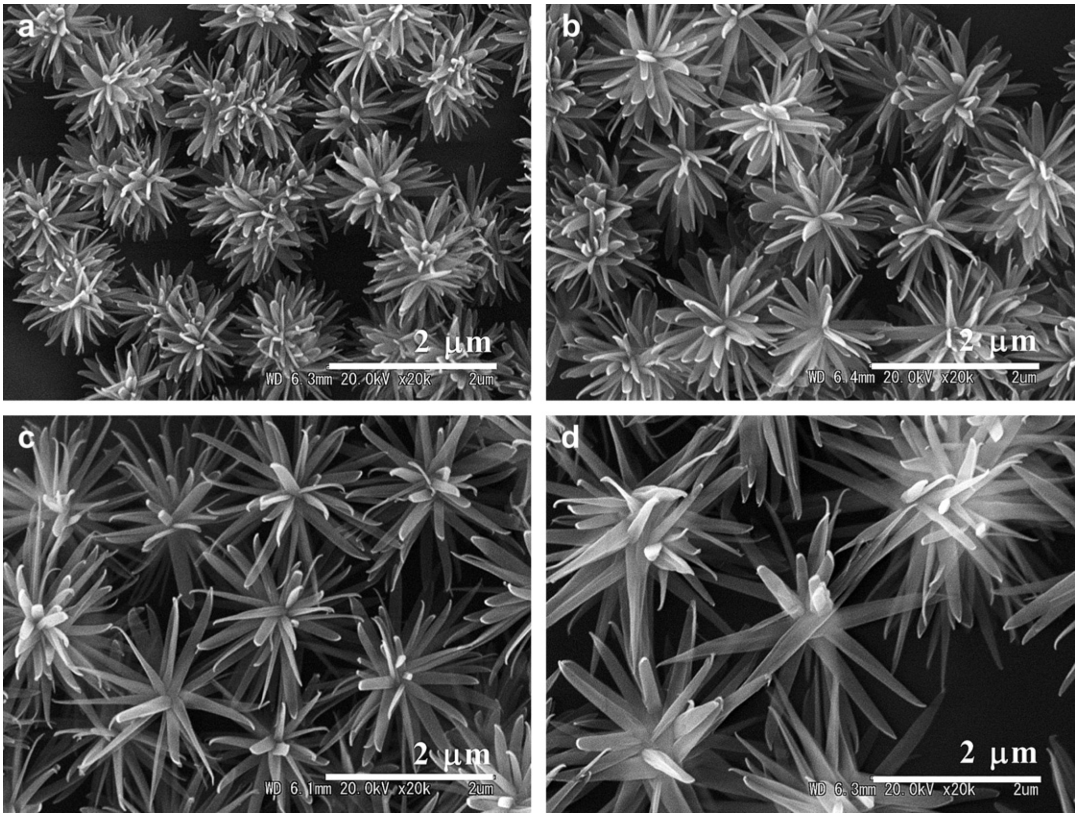


Fig. 5. SEM images of micro-flowers of needle-like PPPI crystals prepared from monomer **1b** at concentrations of (a) 0.1%, (b) 0.25%, (c) 1.0% and (d) 2.0%.

growth rate. It is well known that if the degree of super-saturation is low when the nucleation occurs, the nuclei having larger size are usually formed [19–21]. The larger size of the crystals prepared from monomer **1b** may be attributed to the lower degree of super-saturation of the oligomers prepared from monomer **1b** because of longer alkoxy end-group. The length of the needle-like crystals prepared from monomer **1b** is also larger. This is due to the higher yield of the crystals. The thicknesses of the crystals are almost 20 nm, being not influenced by the structure of monomer and the polymerization concentration. This seems to be attributed to the direction of the crystal growth, and further study is needed to clarify.

Thermal stability of the PPPI needle-like crystals prepared from monomers **1a** and **1b** was estimated on thermogravimetric analysis. Temperatures of 10 wt% loss in N_2 atmosphere were in the range of 598–687 °C as presented in Table 1 and these crystals exhibited excellent thermal stability.

4. Conclusion

Micro-flowers of the PPPI needle-like crystals were prepared by the polymerization of self-polymerizable monomers **1a**, in which the needle-like crystals grew radially from the center part as petals. The average length, width and thickness of the needle-like crystals were 710 nm, 110 nm and 20 nm, respectively. The molecules aligned regularly along the long axis of the needle-like crystal. The polymerization of monomer **1b** also afforded the micro-flowers of the PPPI needle-like crystals at a concentration of 0.15–2.0% with the yield of 86–98%. The sizes of the crystals prepared at a concentration of 0.1% were averagely 660 nm in length and 120 nm in width. Those prepared at a concentration of 2.0% were averagely 1.69 µm in length and 210 nm in width. The thickness was 20 nm. Higher concentration gave longer the needle-like crystals. The size of the flower-like crystals was controllable by the structure of a monomer and the monomer concentration. The micro-flowers possessed high crystallinity and exhibited excellent thermal stability.

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