

Direct Synthesis and Melt-Drawing Property of Aramids by Bulk Polycondensation of Isophthalic Acid with *m*-Phenylenediamine and 3,4'-Oxydianiline

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ABSTRACT: The direct polycondensation of isophthalic acid with a mixture of 1,3-phenylenediamine (*m*-PDA) and 3,4'-diaminodiphenyl ether (3,4'-ODA) could be successfully performed in the bulk to afford the expected co-aramids for the first time. The co-aramids with low molecular weights and 3,4'-ODA contents higher than 50 mol% display excellent thermoplasticity and melt-drawing property. Indeed, several meters long filaments with 12 μm diameter

could be produced. In addition, the environmentally friendly method for the preparation of aramid materials as well as the demonstration of their filament formation will open up the new possibility to prepare aramid fibers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4398–4402, 2012

Key words: high-temperature materials; polycondensation; polyamides; solid-state polymerization; drawing

INTRODUCTION

Wholly aromatic polyamides (aramids), poly(*m*-phenyleneisophthalamide), and poly(*p*-phenyleneterephthalamide) are interesting fiber-forming materials with high maximum-use temperature^{1–5}. The direct synthesis of aramids from diacids and diamines is difficult because of the lower reactivity of aromatic amines compared with that of aliphatic amines. Thus, they are prepared by the solution polycondensation of aromatic diacid chlorides with aromatic diamines, where highly polar aprotic solvents such as *N,N*-dimethylacetamide, *N*-methylpyrrolidone (NMP), and hexamethylphosphoramide are used to prevent precipitation of resulting polymers. Poly(*m*-phenyleneisophthalamide) has excellent flame-resistant properties, and its fiber is produced by solution spinning. A more atom-economical and straightforward method is the direct synthesis of aramids from aromatic dicarboxylic acids and aromatic diamines. Of late, the authors reported the successful direct synthesis of aramids from aromatic dicarboxylic acids and aromatic diamines containing ether linkages using bulk polycondensation⁶. Ether linkages increase the mobility of polymer chains, and decrease the glass transition

temperatures (T_g s) and melting points (T_m s) of the resulting aramids. 3,4'-Diaminodiphenyl ether (3,4'-ODA) is widely used for the synthesis of alternative aramid for poly(*p*-phenyleneterephthalamide)⁷. The melting point of poly(*m*-phenyleneisophthalamide) is 410°C, which is too high for melt spinning. These findings suggested that co-aramids from isophthalic acid (IPA), 1,3-phenylenediamine (*m*-PDA), and 3,4'-ODA would be prepared by a direct polycondensation method in the bulk and their aramid fibers would also be produced by melt spinning, which is a more efficient method than solution spinning.

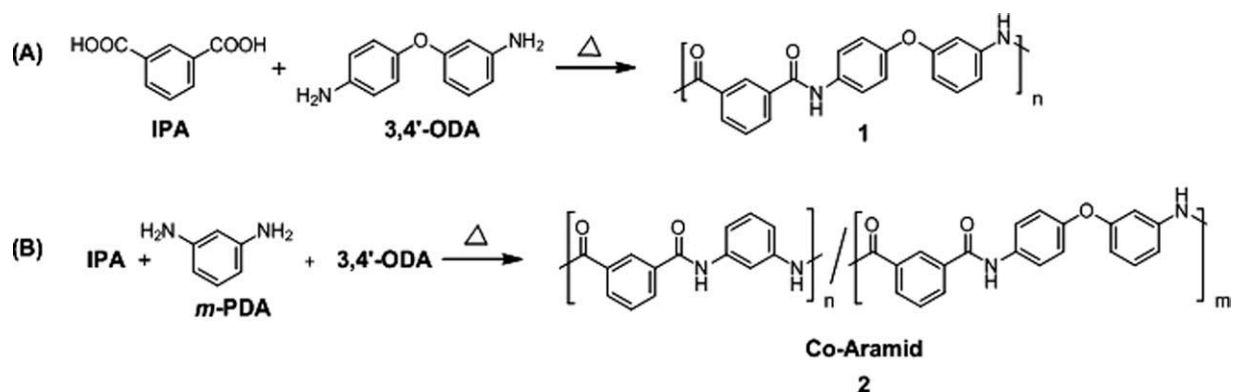
In this study, the authors reported the synthesis of random co-aramids by the bulk polycondensation of IPA with a mixture of 3,4'-ODA and *m*-PDA as well as the possibility of aramid fiber preparation by their melt drawing.

EXPERIMENTAL SECTION

Materials

Isophthalic acid was purchased from TCI, and recrystallized from ethanol before use. *m*-PDA was purchased from Wako Pure Chemical Industries, and purified by sublimation before use. 3,4'-ODA was purchased from TCI, and recrystallized from a mixture of hexane and ethyl acetate (7 : 3 by volume). Other reagents were used as received.

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Scheme 1 (A) Synthesis of aramid 1 from IPA and 3,4'-ODA and (B) synthesis of co-aramid 2 from IPA, 3,4'-ODA and *m*-PDA.

Synthesis of co-aramids

In a typical experiment, IPA (0.166 g, 1.0 mmol), *m*-PDA (0.059 g, 0.55 mmol), and 3,4'-ODA (0.100 g, 0.50 mmol) were placed in a thick culture tube (10 mL) purged with argon.

It was heated at 260°C for 1 h and then at 330°C for 5 h in an electric furnace. After cooling to room temperature, the obtained solid product was dissolved in concentrated sulfuric acid and filtered through a glass filter. The filtrate was then poured into water (500 mL) and NaHCO₃ (30 g) was added to neutralize the solution. The precipitate was collected and washed with water several times, followed by drying at 120°C under vacuum to afford the co-aramid as red powder (0.218 g, 77%). $\eta_{inh} = 0.55$ dL/g. ¹H-NMR (300 MHz, DMSO-*d*₆, δ , 40°C): 10.4 (s, 4H, N-H), 8.54 (d, *J* = 8.4 Hz, 2H, ArH), 8.38 (s, 1H, ArH), 8.20~8.08 (m, 4H, ArH), 7.84 (d, *J* = 8.4 Hz, 2H, ArH), 7.71 (t, *J* = 6.6 Hz, 2H, ArH), 7.55 (d, *J* = 9.3 Hz, 4H, ArH), 7.36 (t, *J* = 7.5 Hz, 2H, ArH), 7.10 (d, *J* = 7.8 Hz, 2H, ArH), 6.78 (d, *J* = 7.5 Hz, 1H, ArH).

Evaluation of viscoelasticity and melt-drawing test

Dynamic viscoelasticity in melt state was measured by rheometer (UBM, RHEOSOL-G3000) with a set of parallel plates under nitrogen atmosphere. The distance between parallel plates was 0.5 mm and applied strain was 0.5°. The frequencies were applied by stepwise pattern as follows. 0.1, 0.2 Hz (with 1.26 rad/s), 0.5, 1, 2 (with 12.6 rad/s), 5, 10 Hz (with 62.8 rad/s), 5, 2, 1, 0.5, 0.2, 0.1, 0.2, 0.5, 1, 2, 5, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.2, 0.5, 1, 2, 5, to 10 Hz. The temperature was set to be 280, 300, and 320°C. The measurement was started after 3 min later from the time when the cell temperature reached the set temperature. Melt-drawing ability was investigated by the method that the parallel plates were separated-off after measuring dynamic viscoelasticity.

Measurements

¹H (300 MHz) spectra were recorded with a Bruker DPX300S spectrometer. The FT-IR spectra were measured by a Horiba FT-720 Fourier transform spectrophotometer. Thermogravimetric analysis was estimated by a Seiko TG/DTA 6300 under nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimetry was estimated using a Seiko DSC 6300 at a heating rate of 10°C/min. Inherent viscosity was determined on 0.5 g/dL concentration of the polymer in concentrated sulfuric acid with an Ostwald viscometer at 30°C.

RESULTS AND DISCUSSION

Synthesis of random co-aramids

In this study, the melt-spinning temperature was set to be around 300°C, at which a melt-spinning equipment of polyester is used. Prior to the synthesis of random co-aramids from IPA, 3,4'-ODA, and *m*-PDA, the bulk polycondensation of IPA with 3,4'-ODA was carried out following a previous study.⁶ The polycondensation proceeded smoothly at 260°C for 2 h and then at 320°C for 5 h, producing the aramid (1) with adequate inherent viscosity of 0.82 dL/g Scheme 1A.

Based on this finding, the bulk copolycondensations of IPA (100 mol%) with a mixture of *m*-PDA (55 mol%) and 3,4'-ODA (50 mol%) were performed at various conditions under nitrogen Scheme 1B to prepare co-aramids (2). Since a co-aramid 2 obtained by the solution polycondensation of isophthaloyl chloride and an equimolar quantity of *m*-PDA and 3,4'-ODA showed the melting point of 327°C, the bulk polycondensation of the same monomers at around 300°C had to be possible. The results are summarized in Table I. The temperature of polymerization was carefully increased in two steps: (i) 260°C for oligomer formation and (ii) above 300°C for increasing molecular weights of co-aramid 2.

TABLE I
Results of Polymerization

Sample	3,4'-ODA content (mol%)	<i>m</i> PDA content (mol%)	Temp. (°C)/time (h)	Yield (%)	η_{inh} (dL/g) ^a	T_g (°C)
2a	50	50	260/1, then 330/5	77	0.55	–
2b	50	50	260/1, then 300/10	87	0.32	253
2c	50	50	260/1	90	0.17	220
2e	25	75	260/1	89	0.13	242
2f	75	25	240/1	90	0.13	214

^a Measured in NMP at 30°C at the concentration of 0.5 g/dL.

The polycondensation proceeded in the melt state at the first step and then in the solid state to yield the desired co-aramid **2** with inherent viscosities up to 0.55 dL/g (**2a**, in Table I). However, co-aramid **2a** with high molecular weights did not show melt-drawing property around 300°C. Thus, co-aramids with low molecular weights were prepared to improve melt-drawing property (**2b** and **2c**, Table I). As shown in Table I, **2a** does not show T_g and the T_g values decrease with decreasing inherent viscosities for **2b** and **2c**.

The chemical structure of aramids was characterized by IR and ¹H NMR spectroscopies. The IR spectra showed characteristic of the N–H and the C=O stretchings of amino and amide carbonyl groups at 3444 and 1658 cm⁻¹, respectively. The representative ¹H NMR spectrum of the co-aramid **2a**, in which a singlet signal **a** assignable to the *o*-aromatic protons next to the amide bond is observed at 8.38 ppm, and the characteristic amide protons at 10.4 ppm appear (Fig. 1). In addition, the characteristic doublet signal **j** at 6.78 ppm is assigned to the *o*-aromatic protons next to the ether linkage. Assignments of other protons are depicted in Figure 1. By comparing the peak intensity of the signals **a** and **j**, the molar composition of *m*-PDA and 3,4'-ODA was determined to be 50/50. Furthermore, the target structures of aramids were also confirmed by elemental analysis.

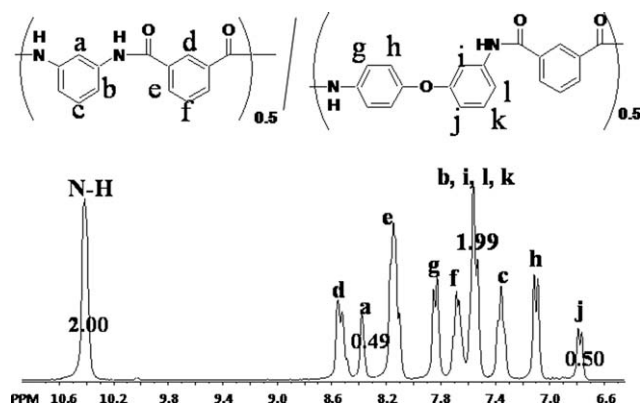


Figure 1 ¹H NMR spectrum of co-aramid **2a**.

Possibility of melt-drawing

Figure 2 shows the relation between hold time and melt viscosity at strain rate of 62.8 rad/s of co-aramids **2** with different compositions. Poly(*m*-phenyleneisophthalamide) even in oligomers does not show any thermoplasticity. The melt viscosity of co-aramids **2e** derived from 3,4'-ODA (25 mol%) and *m*-PDA (75 mol%) rapidly increases with increasing hold time and low thermoplasticity is observed probably because of high contents of rigid *m*-PDA. On the other hand, co-aramids **2c** and **2f** with low molecular weights and 3,4'-ODA contents higher than 50 mol% only show small dependence between hold time and melt viscosity, and exhibit excellent thermoplasticity and melt-drawing property. Furthermore, aramid **1** with an inherent viscosity of 0.22 dL/g also shows excellent melt-drawing ability.

The dependence of melt viscosity on hold time and temperature was then investigated using co-aramids **2c** (Fig. 3). The melt viscosity of **2c** slightly increases by extending the hold time at each temperature, because of the further increase in molecular weights at longer heating time. The melt viscosity of **2c** at 280°C is too high, whereas it decreases with

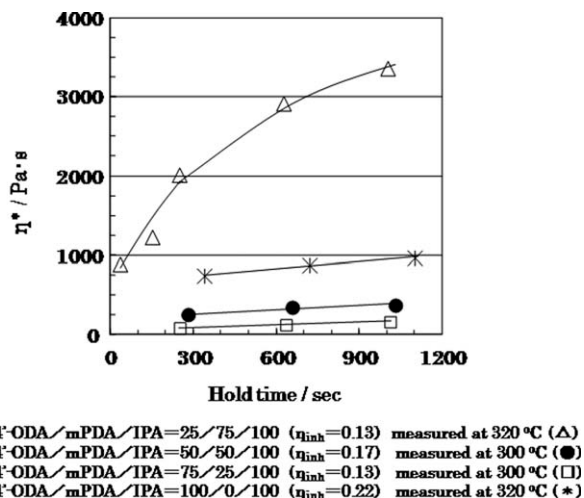


Figure 2 The dependence of melt viscosity on monomer ratio and hold time.

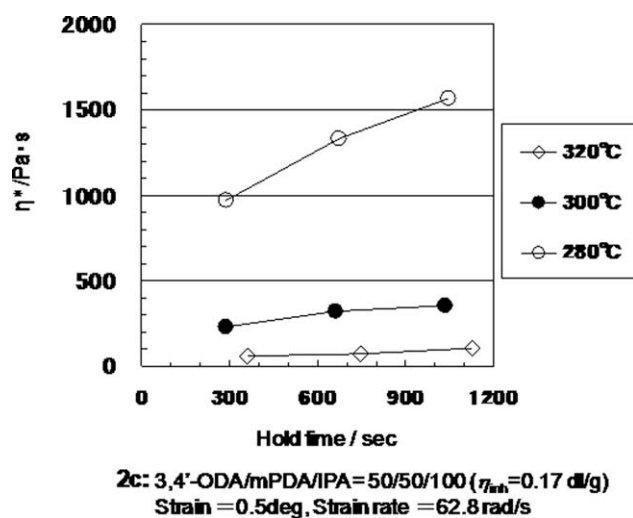


Figure 3 The dependence of melt viscosity on temperature and hold time.

increasing temperature to 320°C, which would become suitable for a melt-drawing process.

Next, melt-drawing possibility of co-aramid **2c** was investigated as summarized in Table II. First, co-aramid **2c** placed between the parallel plates were heated at the set temperature (280, 300, or 320°C) for 20 min and then each plate was taken-off and pulled apart, where the mobile distance between parallel plates is 4 cm. The aramid **2d** without 3,4'-ODA did not show drawing property and thermoplasticity because of strong interaction of polymer chains. The co-aramid **2e** started to show melt-drawing ability, but this ability was poor. In contrast, co-aramid **2c** showed excellent melt-drawing ability. The filaments could be successfully drawn as shown in Figure 4. Furthermore, a fine-stainless needle was put into molten co-aramid **2c**

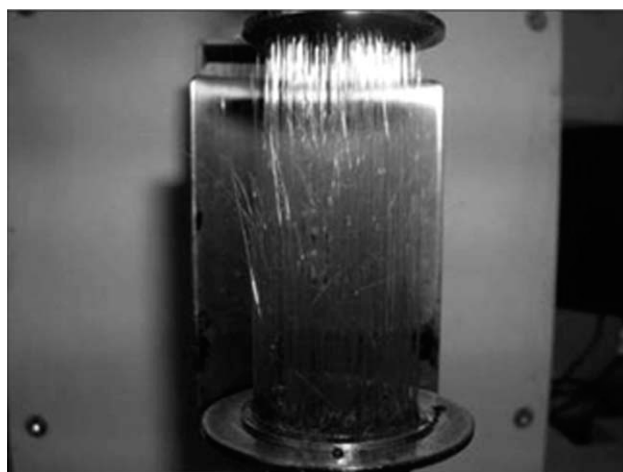


Figure 4 The appearance of melt-drawing ability test.

and draw up them to make a fine filament. Several meters long filament was obtained. Its diameter is only 12 μm as shown in Figure 5, which is thin enough for use in textile industry.

CONCLUSIONS

Random co-aramids **2** from IPA, 3,4'-ODA, and *m*-PDA were successfully prepared by the bulk polycondensation. Co-aramids **2** with low molecular weights and 3,4'-ODA contents higher than 50 mol% exhibit excellent thermoplasticity and melt-drawing property, and produced several meters long filaments with 12 μm diameter. This is the first example of preparation of aramid filaments and this environmentally friendly method can be applied to the preparation of aramid fibers.

TABLE II
Results of Melt-Drawing Property Test^a

Sample ^b	3,4'-ODA content (mol%) ^c	<i>m</i> PDA content (mol%) ^c	η_{inh} (dL/g)	Melt Temp. (°C)	Melt viscosity (Pa.s)	Melt-drawing property
2d	0	100	0.13	320	–	B ^d
2e	25	75	0.13	320	3360	G ^e
2c	50	50	0.17	280	1570	E ^f
2c	50	50	0.17	300	353	E ^f
2c	50	50	0.17	320	105	E ^f

^a Samples were placed between two parallel plates which heated to the set temperature for a while and then pulled.

^b All the samples were prepared by heating the monomers mixture at 260°C for 60 min.

^c Determined by ¹H NMR.

^d Bad: No melt-drawing property and thermoplasticity.

^e Good: Some filaments can be seen around the edge of the plate and shorter than 2 cm.

^f Excellent: The filaments can be seen all over the area of the plate.

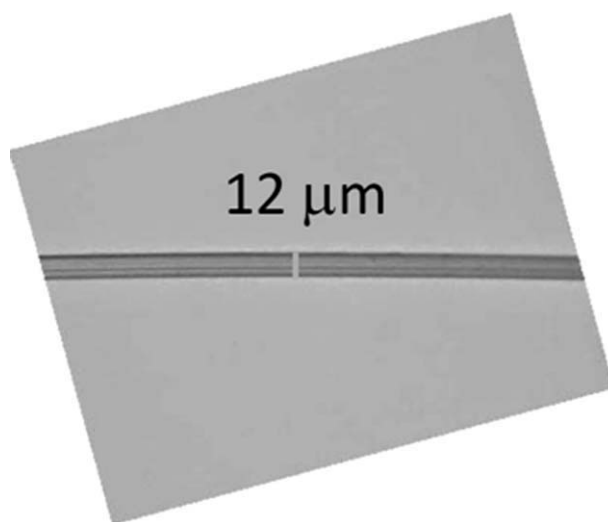


Figure 5 The microscope photograph of a thin filament of co-aramid **2c** obtained by simple drawing method.

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