

SHORT COMMUNICATION

Synthesis of Aramids by Polycondensation of Aromatic Dicarboxylic Acids with Aromatic Diamines Containing Ether Linkages

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Wholly aromatic polyamides (aramids) such as poly(*m*-phenylene-isophthalamide) and poly(*p*-phenyleneterephthalamide) are one of the super engineering plastics, and widely used as fibers with excellent tensile and thermal properties.¹⁻⁴ Aramids are prepared by the solution or interfacial polycondensation of aromatic diacid chlorides with aromatic diamines because of low reactivity of aromatic diamines toward aromatic dicarboxylic acids. Furthermore, some of them are infusible and a melt processing is not possible.⁵ An acid chloride method, however, is not an atom economical one because hydrogen chloride, which has a larger molecular weight than that of water, is produced as a side product. Moreover, a very reactive diacid chloride must be prepared from a dicarboxylic acid with thionyl chloride or other chlorinating agents, and must be stored in a refrigerator under a dry condition to avoid its hydrolysis. Thus, the direct synthesis of aramids from aromatic dicarboxylic acids and aromatic diamines is important and straightforward.

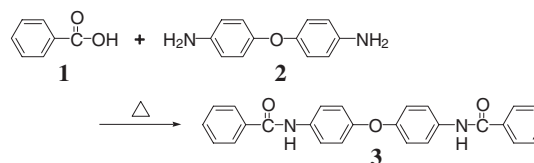
Only one report has been published on the direct synthesis of polyamides using the aromatic diamines.⁶ Holmer and coworkers studied the melt polycondensation of 4,4'-methylenedianiline with aliphatic dicarboxylic acids at around 280 °C under reduced pressure, and reported that high molecular weight polyamides were obtained by using the aliphatic dicarboxylic acids with long methylene units such as nonanedioic acid and decanedioic acid. They also described that some diamines such as 4,4'-oxydianiline and 4,4'-isopropylidenedianiline were degraded in the melt systems used. These findings suggested that some aramids without decomposition would be prepared by a direct polycondensation method.

As the first step for a direct synthesis of aramids, we investigated the synthesis of aramids from aromatic dicarboxylic acids and aromatic diamines containing ether linkages which 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.

Here we report the successful direct synthesis of aramids by the polycondensation of aromatic dicarboxylic acids with aromatic diamines containing ether linkages.

MODEL REACTION

Prior to the synthesis of aramids, the model reaction of benzoic acid (**1**) with 4,4'-oxydianiline (**2**) was carried out in a melt state to investigate the feasibility of the direct synthesis of aramids (Scheme 1). Considering the sublimation of **1**, a small excess amount of **1** to **2** was used. The results are summarized in Table I. All the reactions proceeded at first in homogeneous states and then became heterogeneous after 2 or 3 h depending on the reaction temperature. A quantitative yield of the desired diamide, 4,4'-oxydibenzanilide (**3**) is obtained at 230 °C for 5 h. It is confirmed that an aromatic amine reacts with an aromatic acid in the range of temperature of 200–230 °C.



Scheme 1. Synthesis of diamide **3** from **1** and **2**.

Table I. Synthesis of diamide **3**^a

Run No.	Conditions Temp. [°C]/Reaction time [h]	Yield [%]
1	200/2	58
2	200/5	90
3	230/5	97

^aReaction was carried out with 3.0 mmol of benzoic acid and 1.0 mmol of 4,4'-oxydianiline.

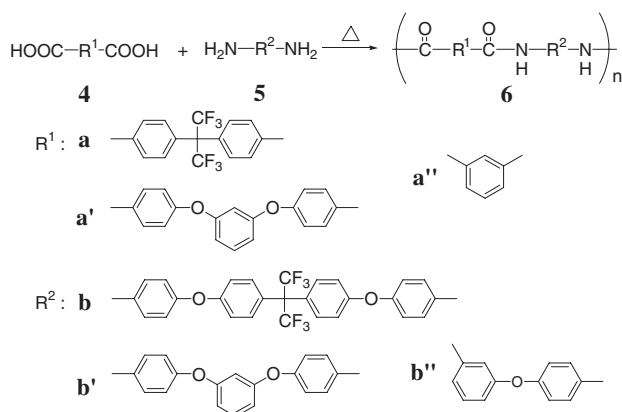
SYNTHESIS OF ARAMIDS

On the basis of the model reaction, the following aramids which were expected to have low melting or low glass transition temperatures due to the presence of flexible ether units were selected. The polycondensations of aromatic dicarboxylic acids, *i.e.*, 4,4'-hexafluoroisopropylidene-bis(benzoic acid) (**4a**), 4,4'-(*m*-phenylenedioxy)-bis(benzoic acid) (**4a'**), and isophthalic acid (**4a''**) with aromatic diamines, *i.e.*, 4,4'-hexafluoroisopropylidene-bis(*p*-phenyleneoxy)dianiline (**5b**), 4,4'-(*m*-phenylenedioxy)dianiline (**5b'**), and 3,4'-oxydianiline (**5b''**) were carried out at various conditions under nitrogen (Scheme 2). The results are summarized in Table II. The temperature of polymerization was carefully increased in three or four steps: (i) above the melting point of diamines to initiate the reaction with dicarboxylic acids, (ii) 170–200 °C for oligomer formation, and (iii) 300 °C for increasing molecular weights of aramids. The polycondensation proceeded in the melt state at the first step and then solid state to yield the desired aramids **6** with high number-average molecular weights (M_n) up to 55,000. Although diamines **5** have a similar ether structure to diamine **2**, aramids with high molecular weights are obtained without degradation of **5**, which is a different result described in the introduction.

The 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 3429 and 1658 cm⁻¹, respectively. Figure 1 shows the ¹H NMR spectrum of aramid

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Scheme 2. Synthesis of aramids **6**.

Table II. Synthesis of aramids **6**^a

R ¹	R ²	Condition	Yield [%]	M _n ^b	M _w ^b	PDI ^b
		Temp. [°C]/Time [h]				
a	b	180/1→200/2→300/7	76	38,000	80,000	2.1
a	b'	130/0.5→170/0.5→200/2→300/7	79	52,000	169,000	3.2
a'	b'	130/0.5→170/0.5→200/2→300/7	77	34,000	71,000	2.1
a''	b'	130/0.5→170/0.5→200/2→300/7	97	55,000	110,000	2.1
a''	b''	100/1→200/2→300/7	91	37,000	116,000	3.1

^aPolycondensation was carried out with 0.5 mmol of each dicarboxylic acid **4** and diamines **5**. ^bDetermined by GPC (DMF, PSt standard).

6ab', in which a doublet signal **2** assignable to the *o*-aromatic protons next to the amide bond is observed at 8.03 ppm, and the characteristic amide protons at 10.4 ppm appear. Assignments of other protons are depicted in Figure 1. Furthermore, the structures of aramids were also confirmed by elemental analysis. These findings clearly supported the formation of the desired aramids **6**.

The thermal properties of aramids **6** were examined by thermogravimetry (TG) and differential scanning calorimetry (DSC) (Table III). Aramids **6** show an excellent thermal stability, and the 5 wt % loss temperatures for polymers are higher than 450 °C under a nitrogen atmosphere. The *T*_gs are above 180 °C. Faint yellow, transparent, and strong films could be obtained by casting from the NMP solutions of aramids **6**.

In summary, we have found that aramids with high molecular weights can be prepared by the direct polycondensation of aromatic dicarboxylic acids and diamines containing ether linkages. This method is applicable for the synthesis of aramids with *T*_gs up to around 250 °C.

Electronic Supporting Information Available: Syntheses and characterization of model compound **3** and polyamide **6ab'**. This material is available via the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>

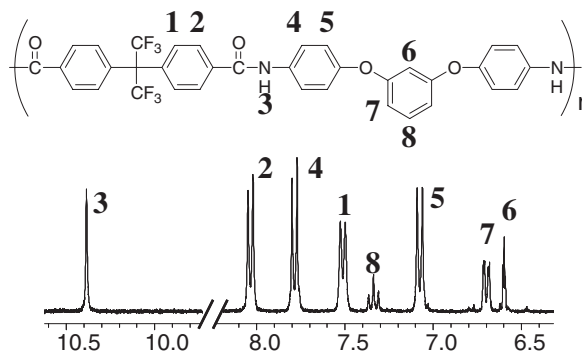


Figure 1. The ¹H NMR spectrum of aramid **6ab'**.

Table III. Thermal properties of aramids **6**

polymer	<i>T</i> _g [°C] ^a	<i>T</i> _m [°C] ^a	<i>T</i> _d [°C] ^b 5 wt % loss
6ab	250	—	460
6ab'	235	—	460
6a'b'	180	300	465
6a''b'	210	340	465
6a''b''	235	—	445

^aMeasured by DSC at a heating rate of 10 °C/min. ^bMeasured by TG at a heating rate of 10 °C/min.

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