

# Synthesis and characterization of aromatic polyamides based on a bis(ether-carboxylic acid) or a dietheramine derived from *tert*-butylhydroquinone

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**SUMMARY:** 1,4-Bis(4-carboxyphenoxy)-2-*tert*-butylbenzene (**2a**) and 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**2b**) were synthesized in two steps starting from the nucleophilic aromatic substitution reaction of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with *tert*-butylhydroquinone in the presence of potassium carbonate in *N,N*-dimethylformamide (DMF). Aromatic polyamides were synthesized by direct polycondensation from diacid **2a** with various diamines or from diamine **2b** with various diacids, by means of triphenyl phosphite and pyridine in *N*-methyl-2-pyrrolidone solution containing calcium chloride. Inherent viscosities of the polyamides ranged from 0.64 to 1.04 dL/g. Almost all the polyamides are readily soluble in various organic solvents and afford transparent and tough films by solvent casting. The polyamides display  $T_g$  values of 209–267 °C and 10% weight loss values above 460 °C in nitrogen and 439 °C in air. A comparative study of some polyamides with an isomeric repeating unit is also presented.

## Introduction

Wholly aromatic polyamides have been noted for their high thermal and chemical resistance as well as high-strength and high-modulus as fibers<sup>1–3</sup>. However, their high softening or melting temperatures and limited solubility in most organic solvents, caused by their rigid structures, make their fabrication difficult. Therefore, current or prior attempts at solubilizing and processing these rigid-chain polymers have been made through the synthetic modification of basic rigid-chain structures by introducing flexibilizing linkages<sup>4–7</sup>, asymmetric units<sup>8–12</sup>, or bulky groups<sup>13–16</sup> into the backbone.

Several previous articles<sup>17–21</sup> have demonstrated that introducing a *tert*-butyl substituted monomer into the polymer backbone improved processability significantly without an unacceptable loss of thermal properties in many aromatic polymer systems such as polyarylates, polyamides, polyimides, and poly(amide-imide)s. The present article describes the successful synthesis of a new ether-linked dicarboxylic acid containing *tert*-butyl-substituted aromatic ring, 1,4-bis(4-carboxyphenoxy)-2-*tert*-butylbenzene (**2a**), and its use for the preparation of polyamides by the direct polycondensation of the diacid with various aromatic diamines. It was hoped that incorporation of *tert*-butyl group into the polymer backbone would disrupt inter-chain hydrogen bonding and reduce packing efficiency and crystallinity. This should promote solubility while maintaining moderate  $T_g$  through controlled segmental mobility. For comparison, some analogous polyamides based on 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**2b**) and aromatic dicarboxylic acids are also prepared and characterized.

## Experimental part

### Materials

*tert*-Butylhydroquinone (*t*-BHQ) (TCI), *p*-fluorobenzonitrile (TCI), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (Wako), potassium hydroxide (Wako), *p*-chloronitrobenzene (TCI) were used without previous purification. *p*-Phenylenediamine (**3a**) (Wako) and *m*-phenylenediamine (**3b**) (TCI) were vacuum-distilled before use. Other diamines including benzidine (**3c**), 4,4'-oxydianiline (**3d**), 4,4'-diaminobenzanilide (**3e**), 4,4'-diaminodiphenylmethane (**3f**), 4,4'-diaminodiphenyl sulfide (**3g**), 1,4-bis(4-aminophenoxy)benzene (**3h**), 1,3-bis(4-aminophenoxy)benzene (**3i**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**3j**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**3k**) and 2,2-bis[4-(4-aminophenoxy)phenyl] sulfone (**3l**) were obtained from TCI and used without further purification. Terephthalic acid (**5a**) (Fluka), isophthalic acid (**5b**) (Fluka), 4,4'-biphenyldicarboxylic acid (**5c**) (TCI), 4,4'-oxydibenzoic acid (**5d**) (TCI), 5-*tert*-butylisophthalic acid (**5e**) (Amoco Chemical Co.), 2,6-naphthalenedicarboxylic acid (**5f**) (TCI), 4,4'-sulfonyldibenzoic acid (**5g**) (New Japan Chemical Co.) and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**5h**) (Chriskev) were also used without further purification. *N,N*-Dimethylformamide (DMF) (Fluka), *N*-methyl-2-pyrrolidone (NMP) (Fluka), *N,N*-dimethylacetamide (DMAc) (Fluka), and pyridine (Py) (Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (TCI) was purified by vacuum distillation. Commercially obtained calcium chloride (Wako) was dried under vacuum at 180 °C for 10 h.

### Monomer synthesis

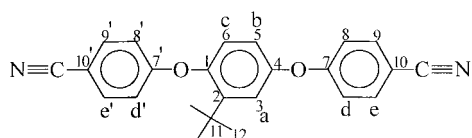
**1,4-Bis(4-cyanophenoxy)-2-*tert*-butylbenzene (1a):** In a 300-mL flask, 16.6 g (0.1 mol) of *t*-BHQ and 27.6 g (0.2 mol) of

$K_2CO_3$  were suspended in a DMF/toluene mixture (100 mL/30 mL), and the suspension was heated at reflux temperature using a Dean-Stark trap to remove the water azeotropically. After complete removal of water, the residual toluene was distilled off. Then, 24.22 g (0.2 mol) of *p*-fluorobenzonitrile was added and heating was continued at 150 °C for 10 h. On cooling, the reaction mixture was poured into 700 mL of water, and the precipitated brown solid was collected and washed with water. The yield of the product was 36.7 g (99.7%). The crude product was purified by recrystallization from methanol/water to afford colorless needles **1a**. The yield of the purified product was 37.1 g (86%); m. p. 112–113 °C.

IR (KBr): 2222 (C≡N str.), 1603–1481 (arom. C=C str.), 1236  $cm^{-1}$  (C—O—C str.).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.60 (dd, 4H,  $H_e + H_e'$ ), 7.13 (s, 1H,  $H_a$ ), 7.00 (dd, 4H,  $H_d + H_d'$ ), 6.87 (s, 2H,  $H_b + H_c$ ), 1.32 (s, 9H,  $-CH_3$ ).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 161.49, 161.45 ( $C^7, C^7'$ ), 150.44 ( $C^4$ ), 150.06 ( $C^1$ ), 144.33 ( $C^2$ ), 134.16, 134.10 ( $C^9, C^9'$ ), 122.82 ( $C^6$ ), 119.98 ( $C^5$ ), 118.88 ( $C^3$ ), 118.67 (cyano carbon), 117.92, 117.55 ( $C^8, C^8'$ ), 105.74 ( $C^{10}, C^{10'}$ ), 34.87 ( $C^{11}$ ), 29.88 ( $C^{12}$ ).



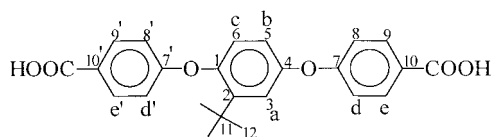
$C_{24}H_{20}N_2O_2$  (368.43) Calc. C 78.24 H 5.47 N 7.60  
Found C 77.92 H 5.66 N 7.59

**1,4-Bis(4-carboxyphenoxy)-2-tert-butylbenzene (2a)**: In a 500-mL flask, a suspension of dinitrile **1a** (30 g, 0.0814 mol) in an ethanol/water mixture (150 mL/150 mL) containing dissolved 46 g (0.814 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 30 h. Reflux was continued for about one day until the evolution of ammonia had ceased. The resulting clear solution was filtered hot to remove any possible insoluble impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH = 2–3. The white precipitated product was filtered off, washed with water, and dried in vacuum, to give 32.62 g (98.6%) of diacid **2a**, m. p. 292–295 °C.

IR (KBr): 2546–2960 (O—H str.), 1689 (C=O str.), 1425–1605 (arom. C=C str.), 1231  $cm^{-1}$  (C—O—C str.).

$^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  = 12.5 (broad, 2H,  $-COOH$ ), 7.95 (d, 4H,  $H_e + H_e'$ ), 7.13 (s, 1H,  $H_a$ ), 7.03 (dd, 4H,  $H_d + H_d'$ ), 6.96 (s, 2H,  $H_b + H_c$ ), 1.28 (s, 9H,  $-CH_3$ ).

$^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  = 166.82 (carbonyl carbon), 161.43, 161.14 ( $C^7, C^7'$ ), 151.30 ( $C^4$ ), 150.15 ( $C^1$ ), 143.27 ( $C^2$ ), 131.78, 131.75 ( $C^9, C^9'$ ), 125.23, 124.98 ( $C^{10}, C^{10'}$ ), 123.18 ( $C^6$ ), 119.21 ( $C^5$ ), 118.82 ( $C^3$ ), 117.08, 116.94 ( $C^8, C^8'$ ), 34.59 ( $C^{11}$ ), 29.80 ( $C^{12}$ ).



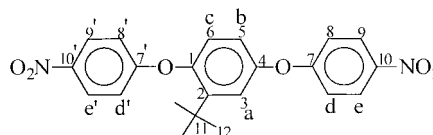
$C_{24}H_{20}O_6$  (406.43) Calc. C 70.93 H 4.96  
Found C 70.18 H 5.55

**1,4-Bis(4-nitrophenoxy)-2-tert-butylbenzene (1b)**: *t*-BHQ (8.31 g, 0.05 mol) and *p*-chloronitrobenzene (14.2 g, 0.101 mol) were dissolved in 70 mL of DMAc. Anhydrous  $K_2CO_3$  (16 g, 0.1 mol) was added to this solution, and the suspension was then refluxed for 6 h. After cooling to room temperature, the product mixture was precipitated into methanol to give a yellow powder. Recrystallization from DMF/methanol gave light yellow crystals (**1b**) that were isolated by filtration, washed with water and dried. The yield was 16.5 g (80%); m. p. 152–153 °C.

IR (KBr): 1516, 1341 ( $NO_2$ ), 1238  $cm^{-1}$  (C—O—C).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.22 (s, 1H,  $H_a$ ), 6.96 (s, 2H,  $H_b + H_c$ ), 7.08 (dd, 4H,  $H_d + H_d'$ ), 8.26 (dd, 4H,  $H_e + H_e'$ ), 1.36 (s, 9H,  $-CH_3$ ).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 163.29, 163.24 ( $C^7, C^7'$ ), 151.42 ( $C^4$ ), 150.74 ( $C^1$ ), 144.70 ( $C^{10}, C^{10'}$ ), 142.81 ( $C^2$ ), 126.13, 126.04 ( $C^9, C^9'$ ), 123.16 ( $C^6$ ), 120.26 ( $C^5$ ), 119.17 ( $C^3$ ), 117.32, 116.98 ( $C^8, C^8'$ ), 34.96 ( $C^{11}$ ), 29.94 ( $C^{12}$ ).



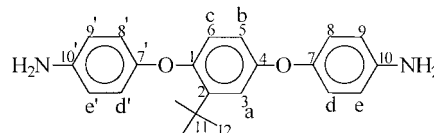
$C_{22}H_{20}N_2O_6$  (408.41) Calc. C 64.70 H 4.94 N 6.86  
Found C 64.56 H 5.15 N 6.46

**1,4-Bis(4-aminophenoxy)-2-tert-butylbenzene (2b)**: The obtained dinitro compound **1b** (16.32 g, 0.04 mol) was refluxed in 110 mL of ethanol in the presence of 10% Pd/C (0.12 g) in a 300-mL three-necked flask. Hydrazine monohydrate (12 mL) was added dropwise to the mixture at 80 °C over a period of 1 h. The mixture was refluxed overnight then filtered hot to remove the catalyst. Upon cooling, white needle-like crystals precipitated (**2b**), that were collected by filtration, recrystallized from ethanol and dried in vacuum. The yield was 12.5 g (90%); m. p. 129–130 °C.

IR (KBr): 3384–3452 (N—H), 1207  $cm^{-1}$  (C—O—C).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.05 (d, 1H,  $H_a$ ), 6.60–6.70 (m, 6H,  $H_b + H_c + H_e$ ), 6.81 (dd, 4H,  $H_d + H_d'$ ), 3.60 (s, 4H,  $-NH_2$ ), 1.40 (s, 9H,  $-CH_3$ ).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 153.35 ( $C^4$ ), 153.22 ( $C^1$ ), 150.30, 149.61 ( $C^7, C^7'$ ), 142.18, 140.83 ( $C^{10}, C^{10'}$ ), 141.74 ( $C^2$ ), 120.26, 119.88 ( $C^8, C^8'$ ), 119.75 ( $C^6$ ), 116.84 ( $C^5$ ), 116.30 ( $C^3$ ), 116.28, 116.23 ( $C^9, C^9'$ ), 34.76 ( $C^{11}$ ), 29.83 ( $C^{12}$ ).



$C_{22}H_{24}N_2O_2$  (348.44) Calc. C 75.83 H 6.94 N 8.04  
Found C 75.66 H 7.31 N 7.56

#### General polymer synthesis

Synthesis of polyamide **4c** is described as a typical procedure. A mixture of 0.406 g (1.0 mmol) of diacid **2a**, 0.184 g

(1.0 mmol) of benzidine (**3c**), 0.3 g of calcium chloride, 0.8 mL of pyridine, 0.6 mL of triphenyl phosphite, and 3 mL of NMP was heated with stirring at 100 °C. After about 1 h, additional 2.5 mL of NMP was added as the solution became too viscous such that the magnetic stirrer could no longer work. After 3 h of stirring at 100 °C, the reaction mixture was poured slowly into 100 mL of stirring methanol, giving rise to a fiber-like precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried under vacuum at 100 °C. The yield was 0.59 g (100%). The inherent viscosity of the polyamide (**4c**) was 1.04 dL/g, as measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

Other polyamides were synthesized in an analogous manner.

### Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N, analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer on KBr disks or solution cast films. NMR spectra were recorded on a Jeol EX-400 FT-NMR spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscometer at 30 °C. DSC traces were obtained on a TA Instruments DSC 2010 at a rate of 20 °C/min in a nitrogen flow (40 cm<sup>3</sup>/min). Thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2050, and experiments were carried out on 10 ± 2 mg samples in flowing nitrogen (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. A LLOYD instrument was used to study the stress-strain behavior of the polymer samples. A gauge length of 2 cm and an extension rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and an average of at least five individual determinations was used.

## Results and discussion

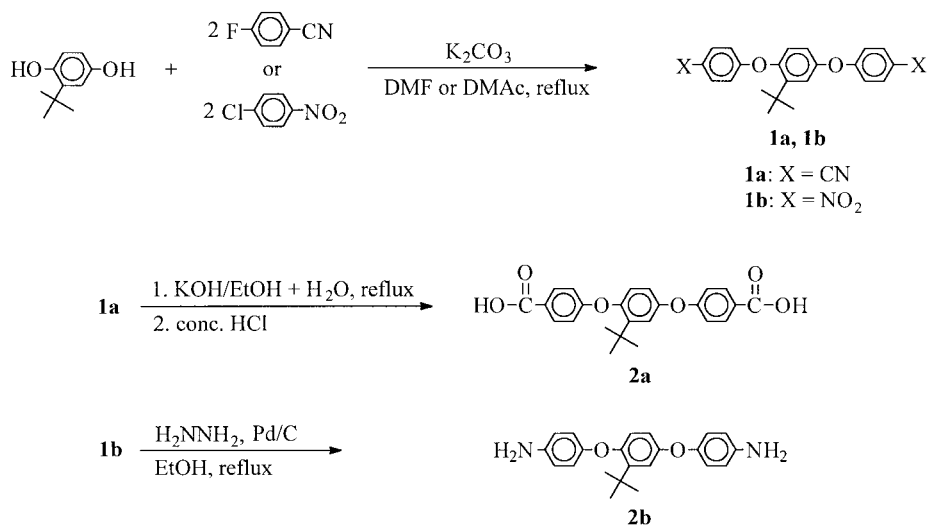
### Monomer synthesis

1,4-Bis(4-carboxyphenoxy)-2-*tert*-butylbenzene (**2a**) and 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**2b**) were prepared in two steps according to Scheme 1. Intermediate compounds **1a** and **1b** were synthesized by nucleophilic aromatic substitution of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with *tert*-butylhydroquinone in the presence of anhydrous potassium carbonate in DMF or DMAc. The dinitrile **1a** was then readily converted into dicarboxylic acid **2a** by alkaline hydrolysis. The diamine **2b** was obtained by reduction of the dinitro compound **1b** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol. All the structures were confirmed by FTIR, NMR and elemental analysis.

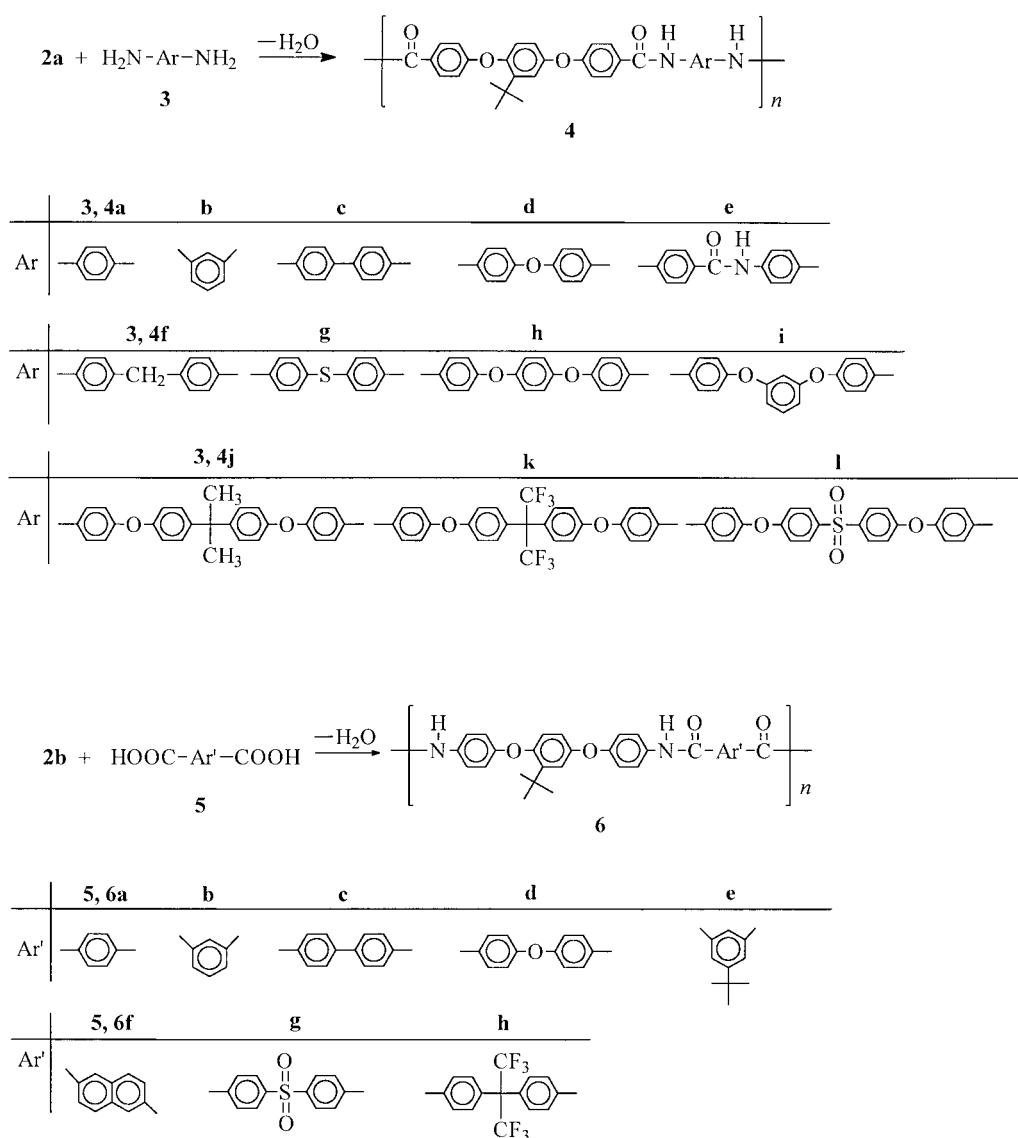
### Polymer synthesis

Two series of aromatic polyamides, **4a–l** and **6a–h**, were synthesized using the Yamazaki<sup>22)</sup> phosphorylation polycondensation procedure from dicarboxylic acid **2a** and diamines **3a–l** and from diamine **2b** and dicarboxylic acids **5a–h** (Scheme 2). All polyamidations proceeded in a homogeneous system throughout the reaction, and the polyamides were isolated as tough fibers in quantitative yields. The synthesis conditions and inherent viscosities of the resulting polyamides are summarized in Tab. 1. Inherent viscosities for **4a–l** ranged from 0.62–1.04 dL/g, and for **6a–h** were between 0.64 and 0.99 dL/g, indicating moderate to high molecular weight polymers. Polymer structures were evidenced by FTIR based on characteristic absorptions around 3300 (N–H stretch),

Scheme 1:



Scheme 2:



2960 (aliphatic C—H stretch), 1650 (C=O stretch), 1510 (N—H bending), 1380 (C—N stretch), and 1220  $\text{cm}^{-1}$  (C—O—C stretch). Elemental analysis of polyamides are shown in Tab. 2. In all cases, the found values were found to be lower than those calculated for the expected structures. This may be attributed to the hygroscopic nature of the amide groups. The corrected values were in agreement with the calculated ones after the absorbed moisture was included.

#### Properties of polymers

The solubility of the polyamides was determined qualitatively (Tab. 3). Polyamides **4** indicated good solubility. Most of them were readily soluble in polar aprotic solvents such as NMP, DMAc, DMF and DMSO, and even

in less efficient ones such as *m*-cresol and pyridine. The polyamides (**4a**, **4c** and **4e**) derived from diamines with a more rigid structure such as *p*-phenylenediamine, benzidine, and 4,4'-diaminobenzanilide showed somewhat lowered solubility. They were soluble in NMP, DMAc and DMSO, but insoluble or just swelling in hot DMF, *m*-cresol and pyridine. Polyamides **6** also exhibited good solubility. Most of them were easily soluble in all tested solvents. Polyamides **6a** and **6c**, from terephthalic acid and 4,4'-biphenyldicarboxylic acid, revealed somewhat poor solubility due to symmetry. In particular, polyamide **6c** was not soluble in polar aprotic solvents without added LiCl, indicating strong hydrogen bonding between chains. Slightly lower solubility for polyamides **6a** and **6c** in comparison to the corresponding **4a** and **4c** having an isomeric repeating segment might be a result of strong

Tab. 1. Synthesis of polyamides

| Polymer   | Amounts of reagents used <sup>a)</sup> |                         |                           |                   | $\eta_{inh}^b$<br>dL/g |
|-----------|--|-------------------------|---------------------------|-------------------|------------------------|
|           | initial NMP<br>in mL                   | additional NMP<br>in mL | CaCl <sub>2</sub><br>in g | pyridine<br>in mL |                        |
| <b>4a</b> | 3                                      |                         | 0.3                       | 0.8               | 0.76                   |
| <b>4b</b> | 2                                      |                         | 0.15                      | 0.6               | 0.62                   |
| <b>4c</b> | 3                                      | 2.5                     | 0.3                       | 0.8               | 1.04                   |
| <b>4d</b> | 2                                      |                         | 0.15                      | 0.8               | 0.70                   |
| <b>4e</b> | 2.5                                    |                         | 0.25                      | 0.8               | 0.98                   |
| <b>4f</b> | 2                                      | 1                       | 0.15                      | 0.6               | 0.79                   |
| <b>4g</b> | 2                                      |                         | 0.15                      | 0.6               | 0.70                   |
| <b>4h</b> | 3                                      | 1                       | 0.25                      | 0.8               | 0.89                   |
| <b>4i</b> | 2                                      | 1                       | 0.15                      | 0.6               | 0.95                   |
| <b>4j</b> | 2.5                                    |                         | 0.25                      | 0.8               | 0.64                   |
| <b>4k</b> | 3                                      |                         | 0.2                       | 0.8               | 0.92                   |
| <b>4l</b> | 3                                      |                         | 0.2                       | 0.8               | 0.70                   |
| <b>6a</b> | 3                                      |                         | 0.3                       | 0.8               | 0.77                   |
| <b>6b</b> | 1.5                                    |                         | 0.15                      | 0.6               | 0.78                   |
| <b>6c</b> | 3                                      |                         | 0.3                       | 0.8               | 0.91 <sup>c)</sup>     |
| <b>6d</b> | 1.5                                    |                         | 0.12                      | 0.6               | 0.99                   |
| <b>6e</b> | 3                                      |                         | 0.15                      | 0.8               | 0.64                   |
| <b>6f</b> | 3                                      |                         | 0.25                      | 0.8               | 0.89                   |
| <b>6g</b> | 2.5                                    |                         | 0.2                       | 0.6               | 0.66                   |
| <b>6h</b> | 1.5                                    |                         | 0.15                      | 0.6               | 0.92                   |

<sup>a)</sup> Polymerization was conducted with 1 mmol of each monomer and 0.6 mL of triphenyl phosphite at 100 °C for 3 h.

<sup>b)</sup> Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>c)</sup> Measured at a concentration of 0.5 g/dL in DMAc + 5 wt.-% LiCl at 30 °C.

Tab. 2. Elemental analysis of polyamides

| Polymer   | Formula<br>(mol. weight)   | Elemental<br>analysis <sup>a)</sup> (%) |       |      | Moisture<br>intake <sup>b)</sup><br>in % |     |
|-----------|--|---|-------|------|--|-----|
|           |  | C                                       | H     | N    |  |     |
| <b>4a</b> | (C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(478.55) <sub>n</sub> | Calc.                                   | 75.30 | 5.48 | 5.85                                     | 7.6 |
|           |  | Found                                   | 69.17 | 5.46 | 5.65                                     |     |
|           |  | Corr.                                   | 74.42 | 5.05 | 6.07                                     |     |
| <b>4b</b> | (C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(478.55) <sub>n</sub> | Calc.                                   | 75.30 | 5.48 | 5.85                                     | 6.8 |
|           |  | Found                                   | 70.25 | 5.53 | 5.83                                     |     |
|           |  | Corr.                                   | 75.03 | 5.15 | 6.22                                     |     |
| <b>4c</b> | (C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(554.65) <sub>n</sub> | Calc.                                   | 77.96 | 5.45 | 5.05                                     | 5.3 |
|           |  | Found                                   | 73.32 | 5.47 | 5.04                                     |     |
|           |  | Corr.                                   | 77.21 | 5.18 | 5.30                                     |     |
| <b>4d</b> | (C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub> ) <sub>n</sub><br>(570.64) <sub>n</sub> | Calc.                                   | 75.77 | 5.30 | 4.91                                     | 5.7 |
|           |  | Found                                   | 71.00 | 5.33 | 4.88                                     |     |
|           |  | Corr.                                   | 75.05 | 5.03 | 5.15                                     |     |
| <b>4e</b> | (C <sub>37</sub> H <sub>31</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub><br>(597.67) <sub>n</sub> | Calc.                                   | 74.36 | 5.23 | 7.03                                     | 6.4 |
|           |  | Found                                   | 69.40 | 5.34 | 6.87                                     |     |
|           |  | Corr.                                   | 73.84 | 5.00 | 7.30                                     |     |
| <b>4f</b> | (C <sub>37</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(568.67) <sub>n</sub> | Calc.                                   | 78.15 | 5.67 | 4.93                                     | 5.3 |
|           |  | Found                                   | 73.63 | 5.64 | 4.78                                     |     |
|           |  | Corr.                                   | 77.53 | 5.34 | 5.03                                     |     |

Tab. 2. Continued

| Polymer   | Formula<br>(mol. weight)  |       | Elemental<br>analysis <sup>a)</sup> (%) |      |      | Moisture<br>intake <sup>b)</sup><br>in % |
|-----------|---|-------|---|------|------|--|
|           |   |       | C                                       | H    | N    |  |
| <b>4g</b> | (C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>n</sub><br>(586.71) <sub>n</sub>               | Calc. | 73.70                                   | 5.15 | 4.77 | 5.9                                      |
|           |   | Found | 68.90                                   | 5.30 | 4.55 |  |
|           |   | Corr. | 72.96                                   | 4.99 | 4.81 |  |
| <b>4h</b> | (C <sub>42</sub> H <sub>34</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub><br>(662.74) <sub>n</sub>                | Calc. | 76.12                                   | 5.17 | 4.23 | 4.2                                      |
|           |   | Found | 72.65                                   | 5.12 | 4.15 |  |
|           |   | Corr. | 75.70                                   | 4.90 | 4.32 |  |
| <b>4i</b> | (C <sub>42</sub> H <sub>34</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub><br>(662.74) <sub>n</sub>                | Calc. | 76.12                                   | 5.17 | 4.23 | 4.6                                      |
|           |   | Found | 72.36                                   | 5.08 | 4.28 |  |
|           |   | Corr. | 75.69                                   | 4.85 | 4.48 |  |
| <b>4j</b> | (C <sub>51</sub> H <sub>44</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub><br>(780.92) <sub>n</sub>                | Calc. | 78.44                                   | 5.68 | 3.59 | 2.4                                      |
|           |   | Found | 76.20                                   | 5.79 | 3.59 |  |
|           |   | Corr. | 78.02                                   | 5.65 | 3.68 |  |
| <b>4k</b> | (C <sub>51</sub> H <sub>38</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub><br>(888.86) <sub>n</sub> | Calc. | 68.92                                   | 4.31 | 3.15 | 1.5                                      |
|           |   | Found | 67.80                                   | 4.31 | 2.91 |  |
|           |   | Corr. | 68.82                                   | 4.24 | 2.95 |  |
| <b>4l</b> | (C <sub>48</sub> H <sub>38</sub> N <sub>2</sub> O <sub>8</sub> S <sub>1</sub> ) <sub>n</sub><br>(802.98) <sub>n</sub> | Calc. | 71.73                                   | 4.73 | 3.48 | 3.3                                      |
|           |   | Found | 69.07                                   | 4.74 | 3.22 |  |
|           |   | Corr. | 71.32                                   | 4.58 | 3.33 |  |
| <b>6a</b> | (C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(478.55) <sub>n</sub>                | Calc. | 75.30                                   | 5.48 | 5.85 | 2.7                                      |
|           |   | Found | 73.17                                   | 5.50 | 5.27 |  |
|           |   | Corr. | 75.14                                   | 5.35 | 5.41 |  |
| <b>6b</b> | (C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(478.55) <sub>n</sub>                | Calc. | 75.30                                   | 5.48 | 5.85 | 3.5                                      |
|           |   | Found | 72.40                                   | 5.53 | 5.14 |  |
|           |   | Corr. | 74.93                                   | 5.34 | 5.25 |  |
| <b>6c</b> | (C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(554.65) <sub>n</sub>                | Calc. | 77.96                                   | 5.45 | 5.05 | 2.6                                      |
|           |   | Found | 75.78                                   | 5.41 | 5.41 |  |
|           |   | Corr. | 77.75                                   | 5.27 | 5.27 |  |
| <b>6d</b> | (C <sub>30</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub> ) <sub>n</sub><br>(570.64) <sub>n</sub>                | Calc. | 75.77                                   | 5.30 | 4.91 | 2.2                                      |
|           |   | Found | 74.13                                   | 5.31 | 4.54 |  |
|           |   | Corr. | 75.76                                   | 5.19 | 4.64 |  |
| <b>6e</b> | (C <sub>34</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(534.65) <sub>n</sub>                | Calc. | 76.38                                   | 6.41 | 5.24 | 2.1                                      |
|           |   | Found | 74.67                                   | 6.42 | 4.73 |  |
|           |   | Corr. | 76.23                                   | 6.29 | 4.82 |  |
| <b>6f</b> | (C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub><br>(528.61) <sub>n</sub>                | Calc. | 77.25                                   | 5.34 | 5.30 | 2.7                                      |
|           |   | Found | 75.01                                   | 5.40 | 4.80 |  |
|           |   | Corr. | 77.03                                   | 5.25 | 5.16 |  |
| <b>6g</b> | (C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> S <sub>1</sub> ) <sub>n</sub><br>(618.70) <sub>n</sub> | Calc. | 69.89                                   | 4.89 | 4.53 | 3.2                                      |
|           |   | Found | 67.38                                   | 4.96 | 4.09 |  |
|           |   | Corr. | 69.53                                   | 4.80 | 4.22 |  |
| <b>6h</b> | (C <sub>39</sub> H <sub>30</sub> N <sub>2</sub> O <sub>4</sub> F <sub>6</sub> ) <sub>n</sub><br>(704.67) <sub>n</sub> | Calc. | 66.48                                   | 4.29 | 3.98 | 1.8                                      |
|           |   | Found | 65.23                                   | 4.37 | 3.51 |  |
|           |   | Corr. | 66.40                                   | 4.29 | 3.57 |  |

<sup>a)</sup> For C and N: Corr. value = found value × (100% + moisture intake %). For H: Corrected value = found value × (100% – moisture intake %).

<sup>b)</sup> Moisture intake (%) = [(W – W<sub>0</sub>)/W<sub>0</sub>] × 100%; W = weight of polymer sample after a prolonged standing at room temperature, and W<sub>0</sub> = weight of polymer sample after drying in vacuum at 100 °C for 10 h.

Tab. 3. Solubility behavior of polyamides<sup>a)</sup>

| Polymer   | Solvent <sup>b)</sup> |      |                     |     |      |                      |    |                                |
|-----------|-----------------------|------|---------------------|-----|------|----------------------|----|--------------------------------|
|           | NMP                   | DMAc | DMAc<br>+5%<br>LiCl | DMF | DMSO | <i>m</i> -<br>Cresol | Py | H <sub>2</sub> SO <sub>4</sub> |
| <b>4a</b> | +                     | +    | +                   | s   | +    | s                    | s  | +                              |
| <b>4b</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4c</b> | +                     | +    | +                   | s   | s    | –                    | –  | +                              |
| <b>4d</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4e</b> | +                     | +    | +                   | s   | +    | –                    | –  | +                              |
| <b>4f</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4g</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4h</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4i</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4j</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4k</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>4l</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6a</b> | +                     | +    | +                   | –   | –    | –                    | –  | +                              |
| <b>6b</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6c</b> | –                     | –    | +                   | –   | –    | –                    | –  | +                              |
| <b>6d</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6e</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6f</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6g</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |
| <b>6h</b> | +                     | +    | +                   | +   | +    | +                    | +  | +                              |

<sup>a)</sup> +, soluble; –, insoluble; s, swelling.

<sup>b)</sup> NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran.

interactions and better packing due to the direct attachment of carbonyl groups on the more rigid aromatic units. In general, polyamides **6** displayed a comparable solubility with **4**, thus supporting that the presence of *tert*-butyl substituent in either diamine or dicarboxylic acid moiety did not affect significantly the polymer solubility. The high solubility of these polyamides is attributed in part to the introduction of bulky *tert*-butyl group into the polymer backbone.

All polyamides except **6c** could be solution-cast into transparent, flexible, and tough films. The tensile properties of these films are given in Tab. 4. These films had tensile strengths of 65–132 MPa, elongations to break of 5–63%, and initial moduli of 1.8–3.6 GPa. Some polyamides such as **4j** and **4k** showed clear yield points in their stress-strain curves and high extensions to break, indicative of high toughness.

The thermal properties of the polyamides were determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Tab. 5. Representative TGA curves of polyamides **4a** and **6a** are shown in Fig. 1. Almost all polyamides showed a similar decomposition behavior and did not degrade noticeably below 450 °C in nitrogen. The 10% weight loss temperatures ranged from 460 to

Tab. 4. Tensile properties of polyamide films<sup>a)</sup>

| Polymer                | Strength at yield in MPa | Strength at break in MPa | Elongation to break in % | Initial modulus in GPa |
|------------------------|--------------------------|--------------------------|--------------------------|------------------------|
| <b>4a</b>              | –                        | 107                      | 10                       | 3.0                    |
| <b>4b</b>              | –                        | 82                       | 5                        | 2.5                    |
| <b>4c<sup>b)</sup></b> | –                        | 120                      | 9                        | 3.6                    |
| <b>4d</b>              | 93                       | 90                       | 13                       | 2.6                    |
| <b>4e<sup>b)</sup></b> | –                        | 132                      | 5                        | 3.6                    |
| <b>4f</b>              | –                        | 85                       | 7                        | 2.2                    |
| <b>4g</b>              | –                        | 92                       | 8                        | 2.3                    |
| <b>4h</b>              | 89                       | 85                       | 30                       | 2.3                    |
| <b>4i</b>              | 95                       | 87                       | 23                       | 2.3                    |
| <b>4j</b>              | 88                       | 86                       | 61                       | 2.0                    |
| <b>4k</b>              | 74                       | 77                       | 63                       | 1.8                    |
| <b>4l</b>              | 95                       | 87                       | 13                       | 2.4                    |
| <b>6a</b>              | –                        | 76                       | 5                        | 2.1                    |
| <b>6b</b>              | 81                       | 65                       | 12                       | 2.4                    |
| <b>6d</b>              | 92                       | 92                       | 30                       | 2.4                    |
| <b>6e</b>              | –                        | 85                       | 7                        | 2.5                    |
| <b>6f</b>              | 95                       | 93                       | 28                       | 2.5                    |
| <b>6g</b>              | 93                       | 85                       | 22                       | 2.2                    |
| <b>6h</b>              | 100                      | 103                      | 35                       | 2.4                    |

<sup>a)</sup> Films were cast from polymer solutions of DMAc.

<sup>b)</sup> Films were cast from polymer solutions of NMP.

Tab. 5. Thermal properties of polyamides

| Polymer   | $T_g^a)$<br>°C | $T_m^b)$<br>°C | $T_{10}/°C^c)$    |        | Char yield <sup>d)</sup><br>in % |
|-----------|----------------|----------------|-------------------|--------|----------------------------------|
|           |                |                | in N <sub>2</sub> | in air |                                  |
| <b>4a</b> | 226            | 367            | 483               | 463    | 57                               |
| <b>4b</b> | 223            | –              | 475               | 454    | 49                               |
| <b>4c</b> | 231            | 417            | 476               | 464    | 55                               |
| <b>4d</b> | 235            | –              | 491               | 474    | 53                               |
| <b>4e</b> | 219            | 410            | 482               | 439    | 47                               |
| <b>4f</b> | 235            | –              | 475               | 479    | 51                               |
| <b>4g</b> | 228            | –              | 460               | 460    | 45                               |
| <b>4h</b> | 224            | –              | 490               | 464    | 47                               |
| <b>4i</b> | 209            | –              | 497               | 464    | 49                               |
| <b>4j</b> | 216            | –              | 493               | 453    | 45                               |
| <b>4k</b> | 226            | –              | 499               | 468    | 50                               |
| <b>4l</b> | 242            | –              | 503               | 479    | 49                               |
| <b>6a</b> | 240            | 375            | 487               | 484    | 58                               |
| <b>6b</b> | 227            | –              | 488               | 486    | 61                               |
| <b>6c</b> | 267            | 433            | 489               | 440    | 60                               |
| <b>6d</b> | 235            | –              | 493               | 467    | 57                               |
| <b>6e</b> | 257            | –              | 495               | 493    | 51                               |
| <b>6f</b> | 233            | 340            | 499               | 484    | 66                               |
| <b>6g</b> | 262            | –              | 478               | 468    | 56                               |
| <b>6h</b> | 261            | –              | 493               | 486    | 56                               |

<sup>a)</sup> Baseline shift in the second heating DSC traces, with a heating rate of 20 °C/min.

<sup>b)</sup> Endotherm peak temperatures observed on the first heating DSC traces at a scan rate of 20 °C/min.

<sup>c)</sup> Decomposition temperatures at which 10% weight loss were recorded by TGA at a heating rate 20 °C/min.

<sup>d)</sup> Residual weight (%) at 800 °C in nitrogen.

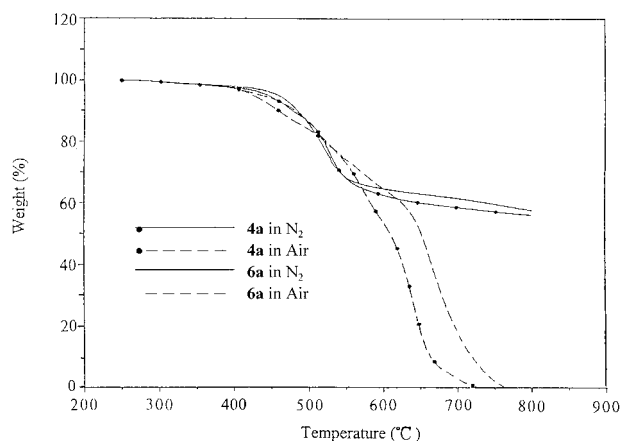


Fig. 1. TGA curves for polyamides **4a** and **6a** with a heating rate of 20°C/min

503°C in nitrogen and 439 to 493°C in air, which are reasonable values considering the aliphatic content of these polyamides. The char yields of these *tert*-butyl group-containing polyamides in nitrogen atmosphere were in the range of 45–66% even at 800°C.

Since the residual water or solvent and the history of thermal annealing may sometimes influence the first run of DSC, samples were at first heated to 450°C and then quenched to room temperature, and  $T_g$  was determined on the subsequent DSC heating trace. Polymers **4a–l** showed  $T_g$  values between 209 and 242°C. The  $T_g$  values for **6a–h** ranged from 227 to 267°C. The  $T_g$  decreased with decreasing rigidity and symmetry of the polymer backbone. A 30°C difference in  $T_g$  between **6b** and **6e** was observed as a result of an increased rotational barrier due to the *tert*-butyl group of diacid **5e**. Introduction of bulky hexafluoroisopropylidene or polar sulfonyl groups generally led to an increase in  $T_g$ . Some polyamides containing a more rigid diamine or diacid residue, such as **5a**, **5c**, **5e**, **6a**, **6c**, and **6f**, exhibited endotherms in the first heating DSC traces. However, rapid cooling and reheating showed a strong  $T_g$  (except **6c**) and disappearance of the melting transitions, pointing at a low crystallization rate. In addition, it is interesting to note that polyamides **6a** and **6c** showed higher  $T_g$  and  $T_m$  values than their corresponding analogs **4a** and **4c**. The only structural difference between these polyamides is the orientation of the amide groups. These results suggest that the attachment of *tert*-butyl in the dicarboxylic acid moiety reduced the chain rigidity.

## Conclusions

Extended dicarboxylic acid **2a** and diamine **2b**, containing *t*-BHQ moiety, were successfully synthesized in high purity and high yields. Polyamides with moderate to high molecular weight were synthesized based on these monomers in good yields. The introduction of *tert*-butyl and aryl ether groups into the backbones of aromatic polyamides improves their solubility without a significant loss of their high thermal properties.

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