

## Preparation of Copolyamides Based on Aramid Blocks with 7–9 Phenylene Monomer Units and Regularly Inserted 1,6-Hexanediamino Units

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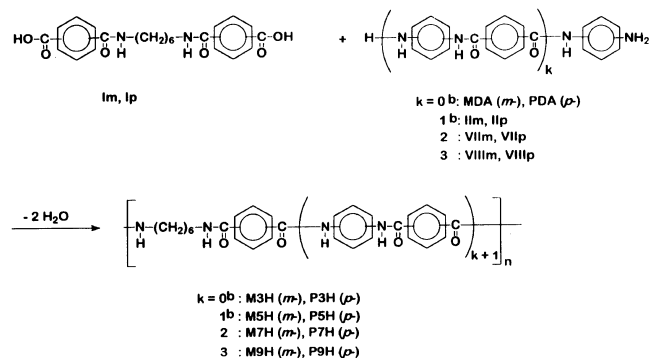
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**ABSTRACT:** Copolyamides based on poly(*m*-phenylene isophthalamide) (PMIA) and poly(*p*-phenylene terephthalamide) (PPTA), to which 1,6-diaminohexane units were regularly inserted every 7 or 9 phenylene monomer units were synthesized. Solubility of the copolyamides was found to be similar to the parent homopolymers PMIA or PPTA.

**KEY WORDS** Nylon / Aramid / Copolymer / Oligoamide / Polycondensation /

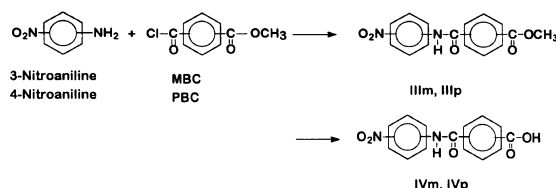
The composition and regularity of a polymer chain deeply influences its ability to crystallize. Strict control of sequence in copolyamides has held our interest as a means of modifying crystallization morphology and kinetics. In a preceding paper,<sup>1</sup> we reported a synthesis of regular copolyamides of poly(*m*-phenylene isophthalamide) (PMIA) or poly(*p*-phenylene terephthalamide) (PPTA) with poly(hexamethylene phthalamide) (Scheme 1). In the present work, preparation of regular block copolyamides based on a longer aromatic amide block will be reported.



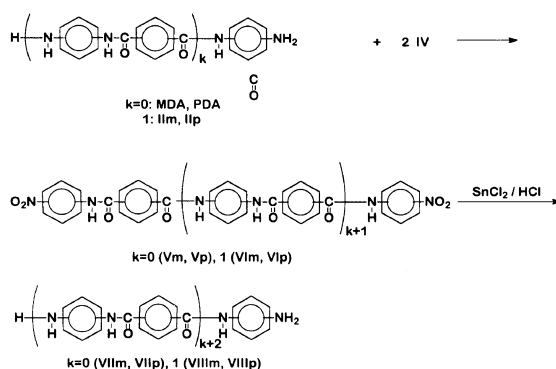
A few block copolymers containing *p*-linked aromatic amide blocks and flexible linkages have been studied mainly in relation with liquid crystallinity. Aharoni prepared strictly alternating rigid-flexible polyamides from 4-aminobenzoic acid and aliphatic dicarboxylic acids, and showed that the lyotropic nature of the polymers is related to the rigid-unit length.<sup>3</sup> More recently, Hyun and Chung<sup>4</sup> synthesized copolyamides based on PPTA and aliphatic dicarboxylic acid and studied their properties. They recognized that the morphology of the copolymer solutions is ruled by the even-odd nature of the methylene units, which controls liquid crystallinity and the formation of solvo-polymer crystals.

In the present work, novel regular block copolyamides composed of aromatic amide blocks with 7–9 phenylene monomer units and a 1,6-hexanediamino units were obtained. The strategy of the synthesis was similar to one reported in a previous paper (Scheme 1). However, larger diamino oligoamide components were needed in order to prepare these copolymers. These proved to be more difficult to prepare. The synthesis of the oligoamides is therefore also included in the present paper (Scheme 2).

(a) Nitrophenyl carboxybenzamides (IV)



(b) Diamino end-capped oligoamides (VII, VIII)



**Scheme 2.** Preparation of diamino end-capped oligoamides.

## EXPERIMENTAL

### Nomenclature

As in the previous paper,<sup>1</sup> *m*- and *p*-substitution of the building blocks were denoted by **m** and **p** after the roman numbers indicating the compounds, respective-

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ly. For copolyamides, *m*-phenylene, *p*-phenylene, and 1,6-hexane monomer units linked together by amide groups were designated as **M**, **P**, and **H**, respectively. Numerical numbers after **M** and **P** refer to the number of phenylene rings between aliphatic chain monomers (see Scheme 1). The parent homopolymers nylon 6I, nylon 6T, PMIA, and PPTA are named **M1H**, **P1H**, **M**, and **P**, respectively.

#### Materials

*m*-Phenylene diamine (MDA) was distilled under vacuum before use. *p*-Phenylene diamine (PDA) was sublimed before use. All other chemicals were used as received.

#### Synthesis of Building Blocks

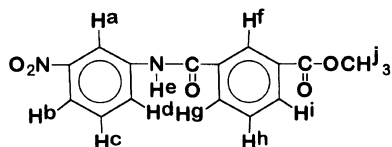
*m*-Methoxycarbonyl benzoyl chloride (MBC), *p*-methoxycarbonyl benzoyl chloride (PBC), and building blocks **Im**, **Ip**, **IIm**, and **Iip** which appear in Scheme 1 were prepared as reported previously.<sup>1</sup>

#### Preparation of *N*-(3-Nitrophenyl) Methoxycarbonyl Benzamide (**IIIIm**)

In a flask, 13.8 g (0.10 mol) of 3-nitroaniline and 100 ml of *N,N*-dimethylacetamide (DMAc) were introduced, and stirred under nitrogen atmosphere. To this, 20 g (0.10 mol) of MBC was added. The stirring was continued for 3 h at room temperature. The solution was poured into water to precipitate the product. The product was washed thoroughly in water, dried under vacuum, and recrystallized from absolute ethanol. The yield was 17 g (57%).

IR (cm<sup>-1</sup>, KBr): 3310 (amide ν(N-H)), 3088 (aromatic ν(C-H)), 1730 (ester ν(C=O)), 1657 (amide I), 1545 (amide II), 1526 (ν<sub>as</sub>(NO<sub>2</sub>)), 1352 (ν<sub>s</sub>(NO<sub>2</sub>)), 1260 (ester ν(C-O)).

<sup>1</sup>H NMR (δ, ppm from tetramethylsilane (TMS) in dimethyl sulfoxide (DMSO)-*d*<sub>6</sub>): 3.90 (s, 3H<sup>j</sup>), 7.62–7.73 (t, 1H<sup>c</sup>; t, 1H<sup>b</sup>), 7.94–7.97 (d, 1H<sup>d</sup>), 8.15–8.21 (d, 1H<sup>e</sup>; d, 1H<sup>f</sup>), 8.23–8.26 (d, 1H<sup>i</sup>), 8.56 (s, 1H<sup>f</sup>), 8.77 (s, 1H<sup>a</sup>), 10.86 (s, 1H<sup>e</sup>).

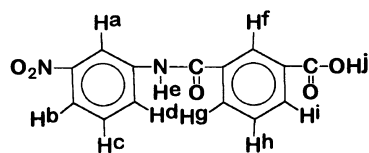


#### Preparation of 3-(3-Nitrophenyl) Carboxybenzamide (**IVm**)

A mixture of 15 g (50 mmol) of ester **IIIIm** and 3.0 g of KOH in 400 ml of water was refluxed for 8 h. The insoluble part was filtrated off, and the free acid was precipitated by adding 38%-HCl. The precipitate was washed with water and dried under vacuum. The yield was 12 g (84%).

IR (cm<sup>-1</sup>, KBr): 3285 (amide ν(N-H)), 3121, 3100 (aromatic ν(C-H)), 1697 (carboxyl ν(C=O)), 1653 (amide I), 1539 (amide II, ν<sub>as</sub>(NO<sub>2</sub>)), 1344 ν<sub>s</sub>(NO<sub>2</sub>).

<sup>1</sup>H NMR (δ, ppm from TMS in DMSO-*d*<sub>6</sub>): 7.62–7.71 (t, 1H<sup>c</sup>, t, 1H<sup>b</sup>), 7.94–7.97 (d, 1H<sup>d</sup>), 8.15–8.22 (d, 1H<sup>e</sup>; d, 1H<sup>f</sup>), 8.57 (s, 1H<sup>f</sup>), 8.79 (s, 1H<sup>a</sup>), 10.86 (s, 1H<sup>e</sup>), 13.32 (s, 1H<sup>j</sup>).

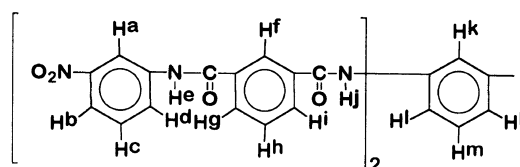


#### Preparation of Dinitro End-Capped Oligoamide with 5 *m*-Phenylene Rings (**Vm**)

In a flask, 5.72 g (20.0 mmol) of **IVm**, 1.08 g (10.0 mmol) of NDA, 40 ml of *N*-methyl-2-pyrrolidinone (NMP), 10 ml of pyridine, 11 ml of triphenyl phosphite (TPP), and 2.0 g of CaCl<sub>2</sub> was placed. The mixture was stirred for 12 h at 100°C under nitrogen atmosphere. The solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly in refluxing methanol, and dried under vacuum. The oligoamide **Vm** was thus obtained with a yield of 5.0 g (78%).

IR (cm<sup>-1</sup>, KBr): 3320, 3283 (amide ν(N-H)), 3121, 3105, 3063 (aromatic ν(C-H)), 1651 (amide I), 1607 (amide II), 1537 (ν<sub>as</sub>(NO<sub>2</sub>)), 1340 (ν<sub>s</sub>(NO<sub>2</sub>)).

<sup>1</sup>H NMR (δ, ppm from TMS in DMSO-*d*<sub>6</sub>): 7.33–7.39 (t, 1H<sup>m</sup>), 7.55–7.57 (d, 2H<sup>l</sup>), 7.65–7.75 (t, 2H<sup>e</sup>; t, 2H<sup>b</sup>), 7.97–7.99 (d, 2H<sup>d</sup>), 8.17–8.20 (d, 2H<sup>e</sup>; d, 2H<sup>i</sup>), 8.23–8.26 (d, 2H<sup>b</sup>), 8.40 (s, 1H<sup>k</sup>), 8.63 (s, 2H<sup>f</sup>), 8.84 (s, 2H<sup>a</sup>), 10.57 (s, 2H<sup>j</sup>), 10.96 (s, 2H<sup>e</sup>).

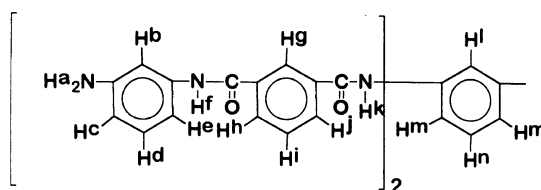


#### Preparation of Diamino End-Capped Oligoamide with 5 *m*-Phenylene Rings (**VIIIm**)

1.9 g (3.0 mmol) of **Vm** was refluxed in 20 ml of absolute ethanol under nitrogen atmosphere. To this, a solution of 4.0 g of SnCl<sub>2</sub>·2H<sub>2</sub>O in 4.0 ml of 38%-HCl was added. The refluxing was continued for an additional 24 h. The solid part was collected by filtration after cooling down, and washed with absolute ethanol. The product was washed successively with NaHCO<sub>3</sub> aq and water, and dried under vacuum. The yield was 0.92 g (52%).

IR (cm<sup>-1</sup>, KBr): 3315 (amide ν(N-H)), 3057 (aromatic ν(C-H)), 1649 (amide I), 1607 (amide II).

<sup>1</sup>H NMR (δ, ppm from TMS in DMSO-*d*<sub>6</sub>): 5.10 (s, 4H<sup>a</sup>), 6.31–6.33 (d, 2H<sup>c</sup>), 6.87–6.90 (d, 2H<sup>e</sup>), 6.95–7.00 (d, 2H<sup>d</sup>), 7.12 (s, 2H<sup>b</sup>), 7.32–7.37 (t, 1H<sup>m</sup>), 7.52–7.55 (d, 2H<sup>m</sup>), 7.64–7.69 (t, 2H<sup>i</sup>), 8.08–8.14 (d, 2H<sup>b</sup>; d, 2H<sup>j</sup>), 8.38 (s, 1H<sup>l</sup>), 8.49 (s, 2H<sup>e</sup>), 10.11 (s, 2H<sup>f</sup>), 10.48 (s, 2H<sup>k</sup>).



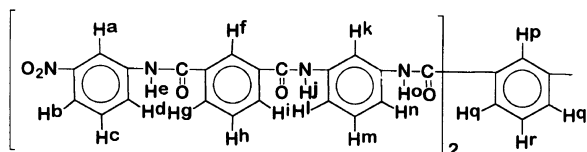
#### Preparation of Dinitro End-Capped Oligoamide with 7 *m*-Phenylene Rings (**VIIm**)

In a flask, 4.29 g (15.0 mmol) of **IVm**, 2.60 g (7.5 mmol)

of **III**m, 40 ml of NMP, 10 ml of pyridine, 11 ml of TPP, and 2.0 g of  $\text{CaCl}_2$  were placed, and stirred for 8 h at  $100^\circ\text{C}$  under nitrogen atmosphere. The solution was poured into methanol, and the oligoamide **VI**m was collected by filtration. The product was washed thoroughly in refluxing methanol, and dried under vacuum. The yield was 5.6 g (85%).

IR ( $\text{cm}^{-1}$ , KBr): 3325 (amide  $\nu(\text{N-H})$ ), 3084 (aromatic  $\nu(\text{C-H})$ ), 1649 (amide I), 1609 (amide II), 1535 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1348 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

$^1\text{H NMR}$  ( $\delta$ , ppm from TMS in  $\text{DMSO-}d_6$ ): 7.34–7.39 (t,  $2\text{H}^{\text{m}}$ ), 7.53–7.56 (d,  $2\text{H}^{\text{l}}$ ; d,  $2\text{H}^{\text{a}}$ ), 7.65–7.75 (t,  $2\text{H}^{\text{c}}$ ; t,  $2\text{H}^{\text{b}}$ ; t,  $1\text{H}^{\text{r}}$ ), 7.97–7.99 (d,  $2\text{H}^{\text{d}}$ ), 8.15–8.24 (d,  $2\text{H}^{\text{b}}$ ; d,  $2\text{H}^{\text{e}}$ ; d,  $2\text{H}^{\text{i}}$ ; d,  $2\text{H}^{\text{a}}$ ), 8.40 (s,  $2\text{H}^{\text{k}}$ ), 8.55 (s,  $1\text{H}^{\text{p}}$ ), 8.59 (s,  $2\text{H}^{\text{f}}$ ), 8.82 (s,  $2\text{H}^{\text{a}}$ ), 10.52 (s,  $2\text{H}^{\text{j}}$ ; s,  $2\text{H}^{\text{o}}$ ), 10.89 (s,  $2\text{H}^{\text{e}}$ ).

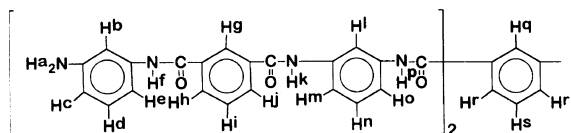


#### Preparation of Diamino End-Capped Oligoamide with 7-*m*-Phenylene Rings (**VIII**m)

In 15 ml of absolute ethanol, 1.77 g (2.0 mmol) of **VI**m was refluxed under nitrogen atmosphere. To this, a solution of 3.3 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and 3.3 ml of 38%  $\text{HCl}$  was added. The refluxing was continued for 16 h. The solid was collected after cooling down, and washed successively in water, sat  $\text{NaHCO}_3$  aq and water. The product was then dried under vacuum. The diamino end-capped oligoamide **VIII**m was obtained with a yield of 0.93 g (56%).

IR ( $\text{cm}^{-1}$ , KBr): 3322 (amide  $\nu(\text{N-H})$ ), 3052 (aromatic  $\nu(\text{C-H})$ ), 1645 (amide I), 1547 (amide II).

$^1\text{H NMR}$  ( $\delta$ , ppm from TMS in  $\text{DMSO-}d_6$ ): 5.12 (s,  $4\text{H}^{\text{a}}$ ), 6.31–6.34 (d,  $2\text{H}^{\text{c}}$ ), 6.87–6.89 (d,  $2\text{H}^{\text{e}}$ ), 6.95–7.00 (t,  $2\text{H}^{\text{d}}$ ), 7.12 (s,  $2\text{H}^{\text{b}}$ ), 7.33–7.38 (t,  $2\text{H}^{\text{n}}$ ), 7.53–7.56 (d,  $2\text{H}^{\text{m}}$ ; d,  $2\text{H}^{\text{o}}$ ), 7.64–7.69 (t,  $2\text{H}^{\text{i}}$ ), 7.68–7.73 (t,  $1\text{H}^{\text{s}}$ ), 8.09–8.17 (d,  $2\text{H}^{\text{h}}$ ; d,  $2\text{H}^{\text{j}}$ ; d,  $2\text{H}^{\text{r}}$ ), 8.39 (s,  $2\text{H}^{\text{l}}$ ), 8.50 (s,  $2\text{H}^{\text{g}}$ ), 8.56 (s,  $1\text{H}^{\text{q}}$ ), 10.12 (s,  $2\text{H}^{\text{f}}$ ), 10.49 (s,  $2\text{H}^{\text{k}}$ ), 10.51 (s,  $2\text{H}^{\text{p}}$ ).

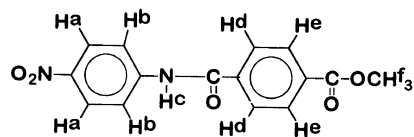


#### Preparation of 4-(4-Nitrophenyl Methoxycarbonyl Benzamide (**III**p))<sup>5</sup>

To a solution of 8.3 g (60 mmol) of 4-nitroaniline in 100 ml of NMP, 12 g (60 mmol) of PBC was added at  $0^\circ\text{C}$  under nitrogen atmosphere with slow stirring. The stirring was continued for 3 h. The product was precipitated by pouring the mixture into water. The precipitate was collected, washed thoroughly in water, and dried under vacuum. The raw product was further purified by recrystallization from absolute ethanol. The yield after recrystallization was 12 g (67%).

IR ( $\text{cm}^{-1}$ , KBr): 3376 (amide  $\nu(\text{N-H})$ ), 3092 (aromatic  $\nu(\text{C-H})$ ), 2968, 2930 (aliphatic  $\nu(\text{C-H})$ ), 1705 (ester  $\nu(\text{C=O})$ ), 1691 (amide I), 1543 (amide II), 1505 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1335 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

$^1\text{H NMR}$  ( $\delta$ , ppm from TMS in  $\text{DMSO-}d_6$ ): 3.89 (s,  $3\text{H}^{\text{f}}$ ), 8.04–8.07 (d,  $2\text{H}^{\text{b}}$ ), 8.10 (s,  $2\text{H}^{\text{d}} + 2\text{H}^{\text{e}}$ ), 8.26–8.29 (d,  $2\text{H}^{\text{a}}$ ), 10.98 (s,  $1\text{H}^{\text{c}}$ ).

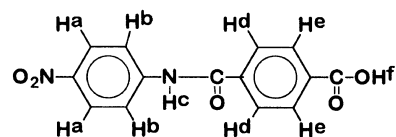


#### Preparation of 4-(4-Nitrophenyl) Carboxybenzamide (**IV**p)

A mixture of 9.1 g (25 mmol) of **III**p, 360 ml of absolute ethanol, and 1.8 g of KOH in 360 ml of water was refluxed with stirring for 2 h. The solution was diluted with water, filtrated, and neutralized with 38%  $\text{HCl}$ . The precipitate was filtrated, washed thoroughly in water, and dried under vacuum. The yield was 6.5 g (75%).

IR ( $\text{cm}^{-1}$ , KBr): 3397 (amide  $\nu(\text{N-H})$ ), 3102 (aromatic  $\nu(\text{C-H})$ ), 1682 (carboxyl  $\nu(\text{C=O})$ ), 1611 (amide I), 1595 (amide II), 1539 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1332 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

$^1\text{H NMR}$  ( $\delta$ , ppm from TMS in  $\text{DMSO-}d_6$ ): 8.04–8.07 (d,  $2\text{H}^{\text{b}}$ ;  $2\text{H}^{\text{d}}$ ;  $2\text{H}^{\text{e}}$ ), 8.25–8.29 (d,  $2\text{H}^{\text{a}}$ ), 10.95 (s,  $1\text{H}^{\text{c}}$ ), 13.25 (s,  $1\text{H}^{\text{f}}$ ).

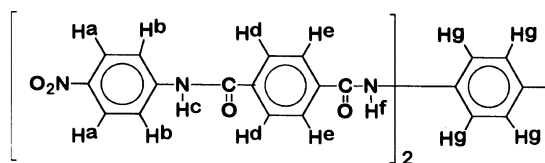


#### Preparation of Dinitro End-Capped Oligoamide with 5-*p*-Phenylene Rings (**V**p)

In a flask, 0.541 g (5.00 mmol) of PDA, 2.86 g (10.0 mmol) of **IV**p, 25 ml of NMP, 2.5 ml of pyridine, 2.6 ml of TPP, and 0.5 g of  $\text{CaCl}_2$  were placed, and stirred at  $100^\circ\text{C}$  for 8 h under nitrogen atmosphere. The mixture was then poured into methanol. The precipitate was collected by filtration, washed thoroughly in refluxing methanol, and dried under vacuum. The oligoamide thus obtained weighed 3.1 g (96%).

IR ( $\text{cm}^{-1}$ , KBr): 3320 (amide  $\nu(\text{N-H})$ ), 3094 (aromatic  $\nu(\text{C-H})$ ), 1647 (amide I), 1545 (amide II), 1503 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1319 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

$^1\text{H NMR}$  ( $\delta$ , ppm from TMS in  $\text{DMSO-}d_6$ ): 7.81 (s,  $4\text{H}^{\text{g}}$ ), 8.09–8.12 (d,  $4\text{H}^{\text{b}}$ ), 8.14 (s,  $4\text{H}^{\text{d}} + 4\text{H}^{\text{e}}$ ), 8.29–8.32 (d,  $4\text{H}^{\text{a}}$ ), 10.89 (s,  $2\text{H}^{\text{f}}$ ), 11.40 (s,  $2\text{H}^{\text{c}}$ ).



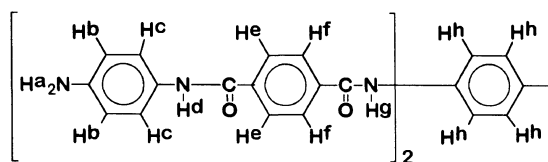
#### Preparation of Diamino End-Capped Oligoamide with 5-*p*-Phenylene Rings (**VII**p)

In a flask, 2.58 g (4.00 mmol) of dinitro compound **V**p was stirred in 30 ml of DMAc at  $100^\circ\text{C}$ . To this, a solution of 12 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 20 ml of conc  $\text{HCl}$  was added. The mixture was stirred at  $100^\circ\text{C}$  for 23 h under nitrogen

atmosphere. The solid part was collected by filtration after cooling down, and successively washed in water sat  $\text{NaHCO}_3$  aq and water. The product was then dried under vacuum. The yield was 1.96 g (84%).

IR ( $\text{cm}^{-1}$ , KBr): 3320 (amide  $\nu(\text{N-H})$ ), 3044 (aromatic  $\nu(\text{C-H})$ ), 1642 (amide I), 1616 (amide II).

$^1\text{H}$  NMR ( $\delta$ , ppm from TMS in  $\text{DMSO}-d_6$ ): 4.96 (s, 4H<sup>a</sup>), 6.53–6.56 (d, 4H<sup>b</sup>), 7.38–7.41 (d, 4H<sup>c</sup>), 7.78 (s, 4H<sup>b</sup>), 8.06 (s, 4H<sup>e</sup> + 4H<sup>f</sup>), 10.02 (s, 2H<sup>d</sup>), 10.39 (s, 2H<sup>g</sup>).

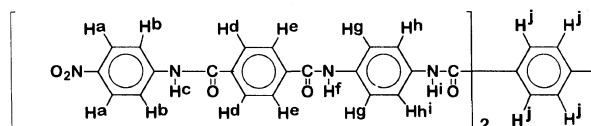


#### Preparation of Dinitro End-Capped Oligoamide with 7p-Phenylene Rings (VIp)

In a flask were placed 1.73 g (5.00 mmol) of **IIp**, 2.86 g (10.0 mmol) of **IVp**, 25 ml of NMP, 5.0 ml of pyridine and 6.0 ml of TPP, which were then stirred at 100°C for 8 h under nitrogen atmosphere. The oligoamide was precipitated in methanol, collected by filtration, washed thoroughly in refluxing methanol, and dried under vacuum. The product weighed 3.1 g (96%).

IR ( $\text{cm}^{-1}$ , KBr): 3331 (amide  $\nu(\text{N-H})$ ), 3053 (aromatic  $\nu(\text{C-H})$ ), 1651 (amide I), 1553 (amide II), 1512 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1325 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

$^1\text{H}$  NMR ( $\delta$ , ppm from TMS in 98%  $\text{D}_2\text{SO}_4$ - $\text{D}_2\text{O}$ ): 7.18 (d, 4H<sup>d</sup> + 4H<sup>e</sup> + 4H<sup>j</sup>), 7.54 (s, 4H<sup>b</sup> + 4H<sup>g</sup> + 4H<sup>h</sup>), 7.71 (s, 4H<sup>a</sup>).



#### Preparation of Diamino End-Capped Oligoamide with 7p-Phenylene Rings (VIIIp)

To a dispersion of 3.53 g (4.00 mmol) of dinitro compound **VIp** in 40 ml of DMAc, a solution of 12 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 20 ml of conc HCl was added at 100°C with stirring. The stirring was continued at 100°C for 23 h under nitrogen atmosphere. The solid part was collected by filtration after cooling down, and successively washed in water, sat  $\text{NaHCO}_3$  aq and water. The product was then dried under vacuum. The yield was 1.96 g (84%).

IR ( $\text{cm}^{-1}$ , KBr): 3322 (amide  $\nu(\text{N-H})$ ), 3052 (aromatic  $\nu(\text{C-H})$ ), 1645 (amide I), 1547 (amide II).

$^1\text{H}$  NMR ( $\delta$ , ppm from TMS in 98%  $\text{D}_2\text{SO}_4$ - $\text{D}_2\text{O}$ ): 6.93 (s, broad, 4H<sup>b</sup>), 7.18 (mult., broad, 4H<sup>c</sup> + 4H<sup>h</sup> + 4H<sup>i</sup>), 7.54 (mult., broad, 4H<sup>e</sup> + 4H<sup>f</sup> + 4H<sup>k</sup>).

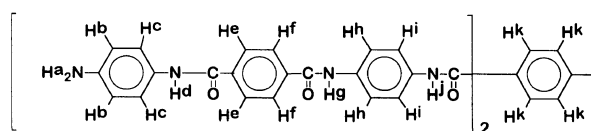


Table I. Preparation of copolyamides

Monomers	Copolyamides			
	$k^a$	Code	Yield %	$\eta_{\text{inh}}^b$ dl g <sup>-1</sup>
<b>VIIIm</b> + <b>IIm</b>	2	<b>M7H</b>	85	0.35
<b>VIIIIm</b> + <b>IIm</b>	3	<b>M9H</b>	100	0.26
MDA + <b>IIm</b>	0	<b>M3H</b>	100	1.14
<b>VIIp</b> + <b>Iip</b>	2	<b>P7H</b>	86	0.14
<b>VIIIp</b> + <b>Iip</b>	3	<b>P9H</b>	67	0.17
PDA + <b>Iip</b>	0	<b>P3H</b>	78	0.083

<sup>a</sup> See Scheme 1. <sup>b</sup> Measured in 98%- $\text{H}_2\text{SO}_4$  at a concentration of 0.5 g dl<sup>-1</sup> at 30°C.

#### Preparation of Copolymers

The preparation procedure was similar for all copolymers, and results are reported in Table I. The following description for **M9H** is given as a representative example.

In a flask equipped with a magnetic stirrer, an oil bath, a refluxing condenser, and a nitrogen inlet were placed 1.65 g (2.00 mmol) of diamine **VIIIm**, 0.824 g (1.00 mmol) of dicarboxylic acid **IIm**, 20 ml of NMP, 5 ml of pyridine, 6 ml of TPP, and 1.0 g of  $\text{CaCl}_2$ . The mixture was stirred at 100°C for 6 h under nitrogen atmosphere. The viscous solution obtained was poured into methanol to precipitate the polymer. The polymer was collected by filtration, washed thoroughly in refluxing methanol, and dried under vacuum. The **M9H** polymer with an inherent viscosity of 0.26 dl g<sup>-1</sup> was obtained with a yield of 2.4 g (100%).

IR ( $\text{cm}^{-1}$ , Film): 3279 (amide  $\nu(\text{N-H})$ ), 3088 (aromatic  $\nu(\text{C-H})$ ), 2934 (aliphatic  $\nu(\text{C-H})$ ), 1655, 1609 (amide I), and 1539 (amide II).

#### Measurements

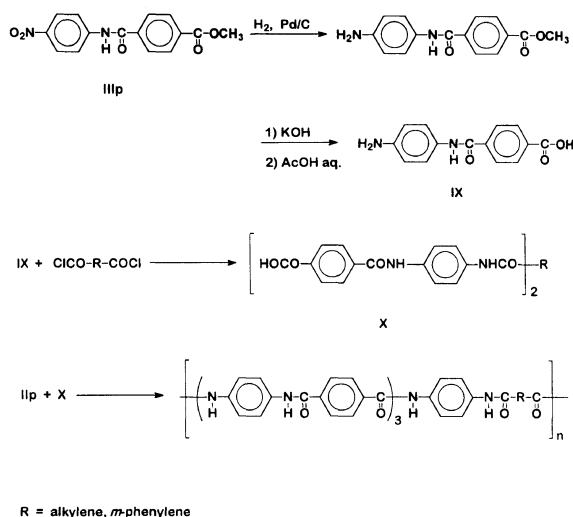
FT-IR spectra were recorded on a Mattson Sirius 100 FT-IR apparatus at a resolution of 4  $\text{cm}^{-1}$ . A total of 200 scans were taken using a MCT detector. Thin films cast from DMAc on KBr disks were used as FT-IR specimens for copolyamides **M7H** and **M9H**. For **P7H** and **P9H**, because of the insolubility in most organic solvents, KBr pellets of powdered polymers were used.

NMR spectroscopy was carried out on a Bruker AC300 apparatus at a frequency of 300 MHz. Deuterated solvents used were  $\text{DMSO}-d_6$  and  $\text{D}_2\text{SO}_4$ , depending on solubility of the compound. Inherent viscosity of the polymers was measured in 98%- $\text{H}_2\text{SO}_4$  at a concentration of 0.5 g dl<sup>-1</sup> at 30°C.

## RESULTS AND DISCUSSION

#### Preparation of Copolyamides

*Strategy* Schemes 1 and 2 show the strategy used to prepare regular copolyamides. This strategy is based on the same principle as described in the previous publication<sup>1</sup>: polycondensation of individually prepared diamino and dicarboxylic-building blocks (Scheme 1). The difference is that larger diamino end-capped polyamide oligomers (**VIIIm**, **VIIp**, **VIIIIm**, and **VIIIp**), prepared as described in Scheme 2, were employed as the diamino

Scheme 3. Procedure of Hyun and Chung.<sup>5,6</sup>

components.

A similar strategy was employed by Hyun and Chung<sup>4</sup> to prepare PPTA-based regular copolyamides (Scheme 3). They utilized  $\alpha,\omega$ -dicarbonyl alkyl or isophthaloyl groups as inserted units, while in the present work 1,6-hexanediamine was used as an inserted diamino units. Accordingly, the strategy of their synthesis was different from ours: they prepared compound **IX** from **IIIp** as shown in Scheme 3,<sup>5</sup> and allowed it to react with diacid chloride to give extended dicarboxylic components **X**.<sup>4</sup> Then **X** were treated with **IIIp** to give the copolymers under a Yamazaki-Higashi condition,<sup>8,9</sup> as in the present case.<sup>4</sup>

#### Building Block Preparation

As described in Scheme 2, the diamino components were constructed by condensation of a *N*-(nitrophenyl)carboxybenzamide (**IVm** or **IVp**) with a smaller diamino component (MDA, PDA, **IIIm** or **IIp**), and subsequent reduction of dinitro end-groups to amino groups. This method is an extension of the strategy used in a previous publication,<sup>1</sup> and also utilized by other researchers<sup>6,7</sup> in order to prepare oligoaramides.

At first, it was attempted to convert **IVm** and **IVp** to corresponding acid chlorides, in order to allow them to react with diamines in the following synthetic steps. However, the purification of acid chlorides of **IVm** and **IVp** turned out difficult because of high reactivity of the compounds. Hence it was decided to use the carboxylic acid form directly for reaction with **MPA**, **PDA**, **IIIm**, and **IIp** using Yamazaki-Higashi condition.<sup>8,9</sup>

The dinitro compounds **Vm** and **VIm** were then treated with  $\text{SnCl}_2/\text{HCl}$  reagent in ethanol following Preston's procedure,<sup>10</sup> to give the diamino end-capped oligoamides. Figure 1 shows the NMR spectra of **VIIIm** and **VIIIIm**. Monodisperse oligoamides were obtained by this method, although conversion of nitrogroups is not 100% complete in **VIIIIm**, as indicated by small residual peaks between 7.7 and 8.1 ppm in the spectrum. This incompleteness is related to the low solubility of large aromatic amide oligomers, which inhibits the reaction to some extent.

Table II reports the composition of *m*-phenylene rings

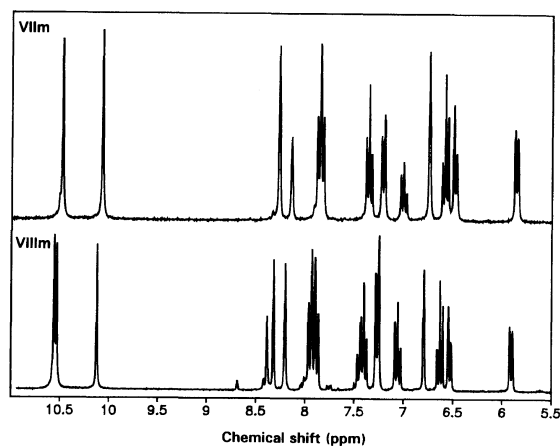
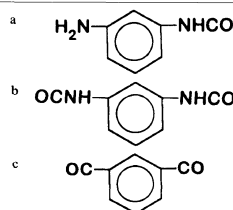


Figure 1. NMR spectra of *m*-substituted diamino end-capped oligoamides.

Table II. Calculation of *m*-phenylene rings content by their substitution types in diamino end-capped oligoamides

Oligoamides		Substitution types			
Code	No. of rings	End <sup>a</sup>	Diamide <sup>b</sup>	Isophthaloyl <sup>c</sup>	
<b>VIIIm</b>	5	Proton <sup>d</sup> Ratio <sup>e</sup>	H <sup>b</sup> (7.12) 1.8 (2)	H <sup>1</sup> (8.38) 1.0 (1)	H <sup>8</sup> (8.49) 1.8 (2)
<b>VIIIIm</b>	7	Proton <sup>d</sup> Ratio <sup>e</sup>	H <sup>b</sup> (7.12) 2.0 (2)	H <sup>1</sup> (8.39) 2.3 (2)	H <sup>8</sup> (8.50), H <sup>9</sup> (8.56) 1.8 (2), 1.0 (1)



<sup>d</sup>Proton used as references (see EXPERIMENTAL section for the assignment). Numbers in parenthesis are the chemical shift.

<sup>e</sup>Number ratio of the *m*-phenylene rings calculated from the NMR integrals. Numbers in the parenthesis are the values calculated for the expected structure.

by substitution types, which were calculated from the NMR integral ratios. The results clearly show that the products contain the phenylene rings of each types in the expected ratios.

The *p*-type dinitro compounds **VIIp** and **VIIIp** were similarly prepared, but DMAc was employed as a reaction medium instead of ethanol for the reduction with  $\text{SnCl}_2/\text{HCl}$  reagent because of the low solubility of the all-*para* aromatic amide oligomers.

NMR spectra of **VIIp** and **VIIIp** are presented in Figure 2. The major observation that can be made when comparing the spectrum of **VIIp** to those of the *meta*-substituted oligomers is that the number of peaks is considerably smaller, due to the higher symmetry of the molecules. Chemical shifts are otherwise similar. The **VIIIp** spectrum is however quite different from the others. Insolubility in organic solvents made NMR characterization difficult for this oligomer, and  $\text{D}_2\text{SO}_4$  had to be used. Because of the high viscosity of this medium, resolution is considerably poorer than for spectra taken in DMSO. Furthermore, because of the

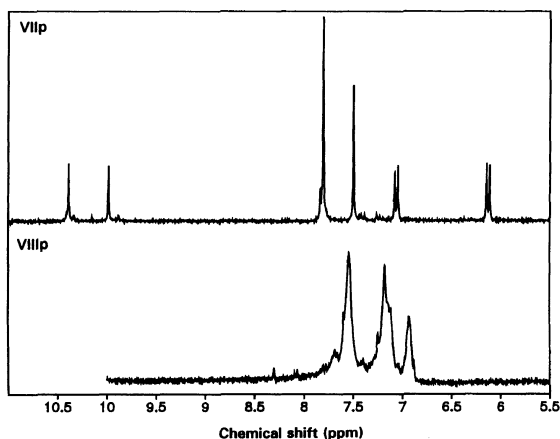


Figure 2. NMR spectra of *p*-substituted diamino end-capped oligoamides.

exchange with  $D_2SO_4$ , peaks appearing near 10.2 ppm, stemming from amide protons, as well as peaks normally appearing near 5 ppm, assigned to  $NH_2$  protons, are absent from the spectra. The aromatic proton region is however consistent with the expected structures, although the chemical shifts are slightly different in  $D_2SO_4$ , as could be expected.

#### Polymerization

The copolyamides were obtained by polycondensation of dicarboxylic components containing an aliphatic unit (**Im** and **Ip**) with diamino aromatic components (**VIIIm**, **VIIIIm**, **VIIp**, and **VIIIp**) via the Yamazaki-Higashi reaction.<sup>8,9</sup> All the copolyamides were obtained with reasonable yields, as shown in Table I.

Molecular weights of the *p*-type copolyamides (**P7H** and **P9H**) were not very high as shown by the low inherent viscosity values (Table I), which is attributed to the low solubility of the polymers.<sup>8,9</sup> However, inherent viscosities of the copolyamides were fairly higher than that of the starting oligoamides: inherent viscosity of **VIp**, the largest *p*-type oligoamide component (dinitro type), was  $0.07 \text{ dl}^{-1} \text{ g}^{-1}$ . This therefore proves that polycondensation has proceeded.

#### Characterization of Copolyamides

The copolyamides **M7H** and **M9H** were soluble in DMAc and 98%  $-H_2SO_4$ , and thus transparent films of these copolyamides were cast from DMAc. On the other hand, copolyamides **P7H** and **P9H** were insoluble in any pure organic solvents and soluble only in 98%  $-H_2SO_4$ . These features are mostly a reflection of the nature of parent homopolymers PMIA (**M**) and PPTA (**P**).

NMR characterization was not carried out for the polymers because of their insolubility in most organic solvents.  $D_2SO_4$  was the only solvent system which could have been used, and it had major drawbacks. Firstly, resolution of the **VIIIp** spectrum in this solvent was already poor, and it would have been even worse for polymer solutions which have a higher viscosity. Secondly, the peaks which are the most interesting in terms of assessing to what extent the reaction has taken place are those due to  $NH_2$  protons. However, as seen in the case of **VIIIp**, these exchange rapidly with  $D_2SO_4$ , and would not be observable.

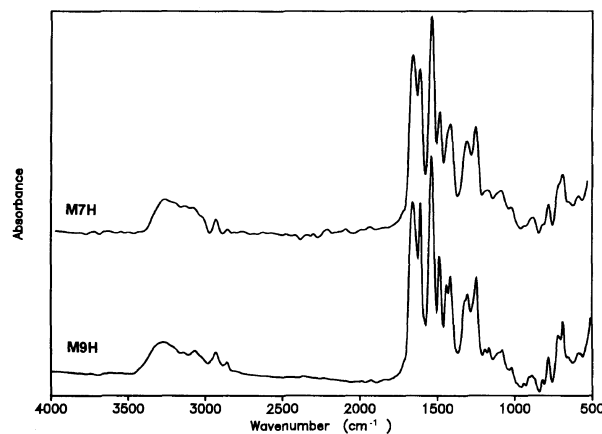


Figure 3. FT-IR spectra (films) of *m*-substituted copolyamides.

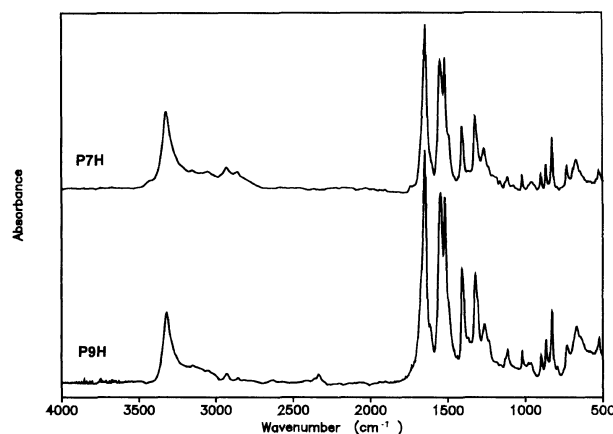


Figure 4. FT-IR spectra (KBr) of *p*-substituted copolyamides.

Therefore, FT-IR was used instead to assess whether the reaction had taken place. Figures 3 and 4 show the FT-IR spectra of the copolyamides obtained. Absorption due to aliphatic C-H stretching (*ca.*  $2930 \text{ cm}^{-1}$ ) is clearly observed in all cases, with an intensity ratio corresponding to the expected stoichiometry as compared to the aromatic C-H stretching absorption vibration (*ca.*  $3080 \text{ cm}^{-1}$ ). This fact confirms that the chemical reaction has taken place between the aliphatic acid and the aromatic oligoamine, and that the composition of the copolyamides alters as designed.

Color of the *p*-type copolymers changed with the aromatic content from white of **PIH** (nylon 6T) to yellow of **P7H**, **P9H**, and **P** (PPTA). PPTA, the all-aromatic *p*-substituted aromatic amide, of which Kevlar® is constituted, is known to be yellow. The color of the copolymers is ascribed to the conjugation in long aromatic amide blocks. On the other hand, *m*-type copolyamides did not show significant color change with composition. The all-aromatic *m*-substituted aromatic amide has a slightly creamy color, which explains that its copolymers do not exhibit striking color changes as compared to nylon 6I.

#### CONCLUSION

As a continuation of the previous work on synthesis of regular copolyamides, copolyamides composed of aromatic amide blocks with 7-9 phenylene monomer

units were prepared. These copolymers were synthesized from diamino oligoamide components (**VII<sub>m</sub>**, **VIII<sub>m</sub>**, **VII<sub>p</sub>**, and **VIII<sub>p</sub>**) and dicarboxylic components (**I<sub>m</sub>** and **I<sub>p</sub>**) via the Yamazaki–Higashi reaction.<sup>8,9</sup> The diamino components were synthesized from smaller diamino monomers (MDA, **II<sub>m</sub>**, PDA, and **II<sub>p</sub>**) and nitro-amide-carboxylic acids (**IV<sub>m</sub>** and **IV<sub>p</sub>**), following the procedure shown in Scheme 2.

Preparation and characterization of the diamino end-capped oligoamides becomes difficult as the size of the molecules enlarges, which is mainly related to their lower solubility.

From FT-IR spectroscopy, the composition of the copolymers was shown to alter as expected. Solubility of the copolymers prepared in this work was similar to the parent homopolymers PMIA and PPTA.

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