

## Synthesis and properties of polyamides and poly(amide-imide)s based on 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline

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### SUMMARY:

The diamines 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (*p*-3 and *m*-3) were synthesized in two steps from the condensation of 4,4'-[1,4(or 1,3)-phenylenediisopropylidene]diphenol (*p*-1 and *m*-1) and *p*-chloronitrobenzene in the presence of  $K_2CO_3$  in *N,N*-dimethylformamide (DMF), giving the corresponding bis(4-nitrophenoxy) compounds, followed by reduction with the hydrazine/Pd-C system. A series of aromatic polyamides, aliphatic-aromatic polyamides, and poly(amide-imide)s were prepared by the direct polycondensation of the diamines with aromatic or aliphatic dicarboxylic acids and phthalimide unit-bearing dicarboxylic acids in *N*-methyl-2-pyrrolidone (NMP) using triphenyl phosphite and pyridine as condensing agents. In addition, two series of polyamides were prepared from terephthalic acid or isophthalic acid and aromatic diamines with isopropylidene and/or other linking groups between the phenylene units, and the structure-property relationships of these polyamides were studied. Almost all the resultant polymers were amorphous in nature and could be solution-cast into transparent, tough, and flexible films. Most of the polymers exhibited moderately high thermal stability. Thus, they are considered as new candidates for processable high-performance polymeric materials.

### Introduction

Aromatic polyimides possess desirable characteristics such as high thermal stability and good mechanical properties<sup>1</sup>. Most of them are rigid rod polymers, and their processing either from the melt or solution is difficult because of their low solubility and high glass-transition or melting temperature<sup>2</sup>. A useful approach to improve the processability without significantly changing their outstanding properties is to introduce groups such as —O—, —SO<sub>2</sub>—, —C(CH<sub>3</sub>)<sub>2</sub>—, —S— into the backbone so as to increase the overall chain flexibility<sup>3,4</sup>.

In the present investigation, the flexible diamines 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (*p*-3 and *m*-3) were synthesized. Although the syntheses of these diamines and a few polyamides derived thereof have been reported in a Japanese patent assigned to the Mitsui Toatsu Chemical Inc.<sup>5</sup>, the characteristics of this kind of condensation polymers are not well understood. In this study, in addition to aromatic polyamides, several aromatic-aliphatic polyamides and some poly-(amide-imide)s on the basis of diamines *p*-3 and *m*-3 will be prepared and characterized by solubility, tensile properties, crystallinity, and thermal properties. The polymers were prepared by a phosphorylation polyamidation route, reported by

Yamazaki et al.<sup>6)</sup>, by means of triphenyl phosphite and pyridine. This route is a very useful laboratory method and has been popularly used in the preparation of polyamides<sup>7-11)</sup> and poly(amide-imide)s<sup>12-16)</sup> directly from diamines with aromatic or aliphatic dicarboxylic acids and imide ring-bearing dicarboxylic acids. Moreover, in order to understand the effects of the length of diamine segment and the linking group on the properties of polyamides, two series of polyamides are prepared from terephthalic acid and isophthalic acid with some aromatic diamines composed of two to five phenylene units connected by ether and/or isopropylidene linkages, and some properties such as solubility and thermal properties of the resultant polyamides are also investigated.

## Experimental part

### Materials

4,4'-(1,4-Phenylenediisopropylidene)diphenol (*p*-1) and 4,4'-(1,3-phenylenediisopropylidene)diphenol (*m*-1) were used as received from Mitsui Petrochemical Ind. (Japan). Hydrazine monohydrate (from Wako), *p*-chloronitrobenzene (from TCI), 10% palladium on activated charcoal (Pd/C) (from Fluka) were used without previous purification.

As described previously<sup>12,17)</sup>, imide-dicarboxylic acids **4o** (m. p. 381 °C, by DSC), **4p** (m. p. 422 °C, by DSC), and **4q** (m. p. 204 °C) were synthesized by condensation of trimellitic anhydride with *p*- and *m*-aminobenzoic acids and 6-aminocaproic acid, respectively. Bis(trimellitimide)s **4r** (m. p. 378 °C, by DSC) and **4s** (m. p. 306 °C, by DSC) were prepared from the condensation of trimellitic anhydride with 4,4'-oxydianiline (TCI) and 1,6-hexanediamine (Wako), respectively, in a molar ratio 1 : 2, according to the method described previously<sup>13)</sup>. All aromatic and aliphatic dicarboxylic acids were of high purity when received from manufacturers and used without any further purification. They include terephthalic acid (**4a**) (Wako), isophthalic acid (**4b**) (Wako), 5-*tert*-butylisophthalic acid (**4c**) (Aldrich), 2,6-naphthalenedicarboxylic acid (**4d**) (TCI), 4,4'-oxydibenzoic acid (**4e**) (TCI), 4,4'-sulfonyldibenzoic acid (**4f**) (New Japan Chemicals Co. Ltd.), 4,4'-(perfluoroisopropylidene)dibenzoic acid (**4g**) (Chriskev), 4,4'-biphenyldicarboxylic acid (**4h**) (TCI), adipic acid (**4i**), pimelic acid (**4j**), suberic acid (**4k**), azelaic acid (**4l**), sebacic acid (**4m**), and dodecanedioic acid (**4n**). (All the aliphatic dicarboxylic acids were purchased from TCI).

4,4'-(1,4-Phenylenediisopropylidene)dianiline and 4,4'-(1,3-phenylenediisopropylidene)dianiline (from Mitsui Petrochemical Ind.) were recrystallized from ethanol prior to use. 4,4'-[Isopropylidenebis(1,4-phenyleneoxy)]dianiline was prepared by condensing *p*-chloronitrobenzene with bisphenol A [4,4'-isopropylidenediphenol] and then reducing the resultant intermediate. 4,4'-(1,4-Phenylenedioxy)dianiline (from TCI) and 4,4'-oxydianiline (from TCI) were used as received.

Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (from TCI) was purified by distillation under reduced pressure.

### Bis[4-(4-nitrophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-2)

Bisphenol *p*-1 (69,3 g; 0,2 mol) and 66,3 g (0,42 mol) of *p*-chloronitrobenzene were dissolved in 200 mL of dried DMF in a 500-mL flask with stirring. Then, 72,2 g (0,52 mol) of anhydrous potassium carbonate was added, and the reaction mixture (which appeared in the form of a suspension) was refluxed at 160 °C for 8 h. The mixture was allowed to cool

and subsequently poured into 600 mL of 1:1 (v/v) methanol-water to precipitate a yellow solid which was collected by filtration and dried. Yield: 115,4 g (98%). The crude product was recrystallized from DMF. Yield: 111,8 g (95%); m. p. 195–197 °C.

IR (KBr): 1568 and 1342  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ), 1296  $\text{cm}^{-1}$  ( $-\text{O}-$ ).

$\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$ (588,67)	Calc.	C 73,45	H 5,48	N 4,76
	Found	C 73,39	H 5,71	N 4,92

#### 4,4'-[1,4-Phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (p-3)

The dinitro compound *p-2* (100 g; 0,17 mol), 0,4 g of Pd/C, 1000 mL of ethanol and 700 mL of tetrahydrofuran (THF) were placed into a 2000-mL flask to which 200 mL of hydrazine monohydrate were added dropwise over a period of 1 h at 85 °C. After the addition was complete, the reaction was continued at reflux temperature for another 10 h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated white crystals were isolated by filtration and dried in vacuum; m. p. 187–189 °C. Yield: 85,4 g (95%).

IR (KBr): 3412, 3344  $\text{cm}^{-1}$  ( $-\text{NH}_2$ ), 1236  $\text{cm}^{-1}$  ( $-\text{O}-$ ).

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 7,10 (t, 8H), 6,73 (d, 8H), 6,57 (d, 4H), 4,95 (s, 4H,  $-\text{NH}_2$ ), 1,57 ppm (s, 12H,  $-\text{CH}_3$ ).

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  = 156,69, 147,34, 145,59, 145,35, 143,49, 127,61, 125,97, 120,86, 115,80, 114,83 (aromatic carbons), 41,42 (quaternary carbon), 30,48 ppm (methyl carbon).

$\text{C}_{36}\text{H}_{36}\text{N}_2\text{O}_6$ (528,69)	Calc.	C 81,79	H 6,86	N 5,30
	Found	C 81,78	H 7,15	N 5,37

#### Bis[4-(4-nitrophenoxy)phenyl]-1,3-diisopropylbenzene (m-2)

The dinitro compound *m-2* was prepared by a similar procedure as *p-2*. Yield: 94%; m. p. 155–156 °C.

IR (KBr): 1589 and 1348  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ), 1270  $\text{cm}^{-1}$  ( $-\text{O}-$ ).

$\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$ (588,67)	Calc.	C 73,45	H 5,48	N 4,76
	Found	C 73,43	H 5,69	N 4,93

#### 4,4'-[1,3-Phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (m-3)

The dinitro compound *m-2* (100 g; 0,17 mol), 0,3 g of Pd/C, and 500 mL of ethanol were placed into a 1000-mL flask to which 130 mL of hydrazine monohydrate were added dropwise over a period of 1 h at 85 °C. After the addition was complete, the reaction was continued at reflux temperature for another 8 h. The mixture was then filtered to remove Pd/C, and 700 mL of  $\text{H}_2\text{O}$  were added after cooling. Subsequently, the product gradually solidified and lumped. After the lumped product was ground, the white powders were collected by filtration and dried in vacuum. Yield: 83,6 g (93%); m. p. 101–103 °C.

IR (KBr): 3456, 3300  $\text{cm}^{-1}$  ( $-\text{NH}_2$ ), 1236  $\text{cm}^{-1}$  ( $-\text{O}-$ ).

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 7,07 (m, 8H), 6,60 (d, 8H), 6,58 (d, 4H), 4,90 (s, 4H,  $-\text{NH}_2$ ), 1,56 ppm (s, 12H,  $-\text{CH}_3$ ).

$^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  = 156,53, 149,67, 145,81, 145,10, 143,52, 127,49, 124,54, 123,65, 120,61, 115,78, 114,81 (aromatic carbons), 41,92 (quaternary carbon), 30,54 (methyl carbon).

$\text{C}_{36}\text{H}_{36}\text{N}_2\text{O}_2$ (528,69)	Calc.	C 81,79	H 6,86	N 5,30
	Found	C 81,80	H 7,18	N 5,40

### Polymerization

A typical example of polymerization was as follows: A mixture of 0,6609 g (1,25 mmol) of diamine *p*-3, 0,2077 g (1,25 mmol) of isophthalic acid (**4b**), 0,1 g of calcium chloride, 0,9 mL of triphenyl phosphite (TPP), 0,8 mL of pyridine, and 2 mL of NMP was heated with stirring at 105 °C for 3 h. As the polycondensation proceeded, the solution became viscous. The obtained polymer solution was trickled into 400 mL of methanol, giving rise to a stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration and dried. The yield was quantitative, the inherent viscosity of the polymer in DMAc containing 5 wt.-% LiCl was 0,89 dL/g, measured at a concentration of 0,5 g/dL at 30 °C.

IR (film): 3 306 (N—H), 1 651 (C=O), 1 228 cm<sup>-1</sup> (—O—).

(C <sub>44</sub> H <sub>38</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (658,80) <sub>n</sub>	Calc.	C 80,22	H 5,81	N 4,25
	Found	C 78,59	H 6,07	N 4,49

All other polyamides and poly(amide-imide)s were synthesized by an analogous procedure as above.

### Measurements

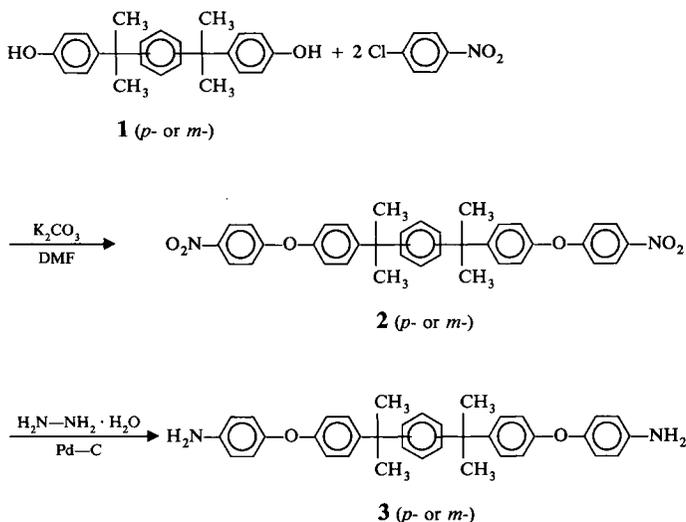
The inherent viscosities were measured with a Cannon-Fenske viscosimeter thermostated at 30 °C. Weight-average molecular weight ( $\bar{M}_w$ ) and number-average molecular weight ( $\bar{M}_n$ ) were determined by means of gel-permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0,01 mol/L of lithium bromide). IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were performed using a Perkin-Elmer C, H, N 2400 elemental analyzer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined at 30 °C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as an external reference, working at 400 and 100 MHz, respectively. The DSC traces were measured on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at the heating rate of 20 °C/min in flowing nitrogen (30 cm<sup>3</sup>/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. The measurements were taken after an initial 250 °C/5 min drying step. The wide-angle X-ray scattering measurements were performed at room temperature (about 25 °C) with film specimens of about 0,1 mm thickness with a Rigaku Geiger Flex D-Max III<sub>a</sub> X-ray diffractometer, using Ni-filtered CuK<sub>α</sub> radiation (operating at 40 kV and 15 mA). The scanning rate was 2 °/min over a range of 2θ = 5–40°. Tensile properties were determined from stress-strain curves obtained by an Instron universal tester Model 1130 with a load cell of 5 kg. A gauge of 2 cm and an elongation rate of 5 cm/min were used for this study. The measurements were performed at room temperature using solution-cast film specimens (0,5 cm wide, 6 cm long, and about 0,1 mm thick), and an average of at least five individual determinations was used.

## Results and discussion

### Monomer synthesis

The diamines *p*-3 and *m*-3 were synthesized in two steps starting from their bisphenol precursors and *p*-chloronitrobenzene (*Scheme 1*). In the first step, 4,4'-[1,4(or 1,3)-

Scheme 1:



phenylenediisopropylidene]diphenol (*p*- or *m*-1) and *p*-chloronitrobenzene were condensed in the presence of a base such as  $\text{K}_2\text{CO}_3$  in an aprotic polar solvent like DMF, giving rise to the corresponding bis(4-nitrophenoxy) compounds **2**. The intermediate dinitro compounds **2** were then catalytically reduced to the desired diamines *m*- and *p*-**3** using hydrazine as the reducing agent and palladium as the catalyst. The yield was high (93–95%), and the purity was also high enough for the preparation of polymers with high molecular weights. The structures of intermediate dinitro compounds **2** and diamines **3** were confirmed by elemental analysis, FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, and the results were in good agreement with proposed structures.

### Polymer synthesis

The direct polycondensation of aromatic diamines with dicarboxylic acids using triphenyl phosphite as condensing agents is a convenient method for the preparation of polyamides on a laboratory scale. Several aromatic polyamides **5a–h**, aliphatic-aromatic polyamides **5i–n**, and poly(amide-imide)s **5o–s** were prepared from diamines *p*- and *m*-**3** with aromatic dicarboxylic acids **4a–h**, aliphatic dicarboxylic acids **4i–n**, and phthalimide unit-bearing dicarboxylic acids **4o–s**, respectively, by the direct polycondensation technique (Scheme 2). The characteristics of all the obtained polymers are summarized in Tab. 1.

The inherent viscosity values of *p*-**5** series polymers derived from diamine *p*-**3** were in the range of 0,64–1,20 dL/g. Aromatic polyamide *p*-**5h**, derived from 4,4'-biphenyldicarboxylic acid (**4h**), was insoluble in the eluent of GPC and its molecular weight data were not obtained. All other *p*-series polymers were soluble in the eluent,



and their  $\bar{M}_w$  values were recorded between 47 000–159 000. Diamine *m-3* had lower tendency to crystallize, so that we failed to acquire *m-3* of higher purity by means of crystallization. As a result, the *m-5* series polyamides were produced with lower  $\eta_{inh}$  values and lower average molecular weights than the corresponding *para* isomeric polymers; their  $\eta_{inh}$  and  $\bar{M}_w$  values were in the range of 0,38–0,88 dL/g and 35 000–108 000, respectively. From the  $\eta_{inh}$  and  $\bar{M}_w$  values, it is evident that the  $\eta_{inh}$  values of these polymers depend not only upon their molecular weights, but also upon the structures of polymers. For example, the polyamides *p-* or *m-5b* and *p-* or *m-5c* derived from *meta*-linked dicarboxylic acids (e. g., **4b** and **4c**) had lower  $\eta_{inh}$  values than the polyamides *p-* or *m-5a* derived from the corresponding *para*-linked dicarboxylic acid (e. g., **4a**); however, the former exhibited a relatively higher average molecular weight. Aromatic polyamides *p-* or *m-5a* and *p-* or *m-5b* with inherent viscosities of 1,25, 0,74, 0,83, and 0,63 dL/g, respectively, were also successfully obtained by the low-temperature solution polycondensation. This indicates that this method may afford polymers with comparable inherent viscosities compared with the ones obtained by direct polycondensation. However, the diacyl chlorides require a troublesome process of purification before use and need to be stored with care.

The formation of polyamides and poly(amide-imide)s was confirmed by elemental analysis and IR spectroscopy. Elemental analyses are in good agreement with the proposed structures, except the values found for the C-percentages, which are always lower than the theoretical ones. That certainly can be due to the distinct aromatic nature of these polymers which commonly leave a small coal residue in the standard conditions of microanalysis. On the other hand, water absorption could also give rise to slight differences in the values of elemental analyses. The IR spectra of the polyamides showed characteristic amide absorptions near 3 300  $\text{cm}^{-1}$  (N—H) and 1 670  $\text{cm}^{-1}$  (C=O), and those of the poly(amide-imide)s showed additional characteristic imide ring absorptions near 1 780  $\text{cm}^{-1}$  (asym. C=O stretching of imide ring), 1 720  $\text{cm}^{-1}$  (sym. C=O stretching of imide ring), 1 390  $\text{cm}^{-1}$  (C—N), and 725  $\text{cm}^{-1}$  (imide ring deformation).

### *Properties of polymers*

A qualitative determination of the solubility of all the polymers was carried out in various solvents. All the polymers were readily soluble in NMP and also in DMF and DMAc except for polymers *p-5h* and *m-5a*. The less solubility of *p-5h* and *m-5a* may be due to their partially crystalline nature, as evidenced by the DSC measurements. Most polymers were only partially soluble in DMSO. Most of polymers, especially for the aliphatic dicarboxylic acid-derived polyamides, showed good solubility even in *m*-cresol and tetrahydrofuran. The good solubility behavior of these polymers may be attributed in part to the introduction of flexible isopropylidene and ether connecting groups in the polymer backbone.

The X-ray diffraction studies of the polymers evidenced that almost all the polymers were amorphous. Almost all the polymers, except for *m-5a*, *p-5h*, and *m-5o*, could be cast into transparent, tough, and flexible films by evaporation of their polymer solutions in DMAc. The tensile strength, elongation to break, and tensile modulus of the

Tab. 1. Characteristics of polyamides and poly(amide-imide)s<sup>a)</sup>

Polymer	$\eta_{inh}^{b) c)}$ dL/g	$\bar{M}_w^{d)}$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$T_g/^\circ C^e)$	$T_d/^\circ C^f)$		Char residue <sup>g)</sup> in wt.-%
					in air	in N <sub>2</sub>	
<i>p</i> -5a	1,20 (1,25)	10,9	2,10	224	485	497	47,5
<i>p</i> -5b	0,89 (0,83)	15,1	2,16	217	482	493	44,8
<i>p</i> -5c	0,64	13,6	2,13	237	512	493	50,5
<i>p</i> -5d	1,17	15,9	2,41	235	480	506	58,2
<i>p</i> -5e	0,75	9,7	2,06	223	475	483	56,3
<i>p</i> -5f	0,80	10,2	2,32	242	477	479	49,3
<i>p</i> -5g	0,77	8,3	2,86	227	501	476	41,4
<i>p</i> -5h	0,89	—	—	230 (352) <sup>h)</sup>	469	481	55,0
<i>m</i> -5a	0,73 (0,74)	8,0	2,29	175 (303)	516	507	51,4
<i>m</i> -5b	0,52 (0,63)	9,5	2,44	180	505	484	53,9
<i>m</i> -5c	0,54	10,8	2,40	207	502	480	46,8
<i>m</i> -5d	0,80	8,6	2,97	175 (267)	514	492	56,7
<i>m</i> -5e	0,83	13,6	2,09	180	491	478	48,2
<i>m</i> -5f	0,78	8,0	2,35	201	477	455	48,9
<i>m</i> -5g	0,62	7,4	2,31	200	498	483	37,3
<i>m</i> -5h	0,82	6,6	2,64	212 (370)	479	463	51,7
<i>p</i> -5i	0,95	9,9	2,25	160	407	410	19,6
<i>p</i> -5j	0,87	4,7	1,52	155	453	429	12,0
<i>p</i> -5k	0,95	12,8	2,50	152	466	439	5,0
<i>p</i> -5l	0,82	8,7	2,23	146	475	449	8,0
<i>p</i> -5m	1,01	13,1	2,52	144	474	460	18,2
<i>p</i> -5n	0,84	8,4	2,27	130	463	445	4,7
<i>m</i> -5i	0,54	5,0	1,92	103	415	407	12,6
<i>m</i> -5j	0,41	4,2	1,75	82	440	433	20,8
<i>m</i> -5k	0,42	3,5	1,94	79	456	444	13,3
<i>m</i> -5l	0,38	4,9	1,88	61	462	455	27,0
<i>m</i> -5m	0,44	4,8	1,92	87	474	460	18,2
<i>m</i> -5n	0,51	5,2	2,00	85	468	463	17,3
<i>p</i> -5o	0,87	6,2	2,38	245	483	482	56,7
<i>p</i> -5p	0,85	11,0	2,50	240	504	498	57,0
<i>p</i> -5q	0,99	12,7	2,59	182	461	457	49,0
<i>p</i> -5r	0,65	5,5	2,29	240	520	503	54,4
<i>p</i> -5s	0,97	7,4	2,47	190	486	487	54,0
<i>m</i> -5o	0,62	6,2	2,30	203	467	471	58,4
<i>m</i> -5p	0,54	5,5	2,29	201	506	496	58,4
<i>m</i> -5q	0,79	6,3	2,33	148	424	416	48,3
<i>m</i> -5r	0,50	4,1	2,16	205	528	517	55,0
<i>m</i> -5s	0,88	5,8	2,32	165	456	457	45,5

a) Polymerization was carried out with 1,25 mmol of each monomer, 2,50 mmol of TPP, 1 mL of pyridine, and 0,4 g of CaCl<sub>2</sub> in 2–5 mL of NMP at 105 °C for 3 h.

b) Intrinsic viscosity measured at 0,5 g/dL in DMAc containing 5 wt.-% LiCl dissolved, at 30 °C.

c) Values in parentheses are for the polyamides obtained via low temperature solution polycondensation from terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC)

with diamines *p*-3 or *m*-3 in NMP. Reaction conditions: amount of TPC or IPC = amount of diamines *p*-3 or *m*-3 = 1,25 mmol, NMP vol. = 5 mL, temperature = -5 to 0 °C, time = 1 h.

- d) Determined by GPC.
- e) Glass transition temperature from the second heating traces of DSC measurements conducted at a heating rate of 20 °C/min in N<sub>2</sub>.
- f) Decomposition temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 20 °C/min.
- g) Char residue at 800 °C in nitrogen.
- h) Values in parentheses are the endothermic peak temperatures observed on the first heating DSC trace, with a heating rate of 20 °C/min.

films were 26–75 MPa, 3–22%, and 0,98–1,95 GPa, respectively. Some *para* isomeric polymers showed yield points on their stress-strain curves. The lower molecular weights developed by the *meta*-isomeric polymers and the effect of molecular disorder were most likely responsible for the lower mechanical strength and elongation to break.

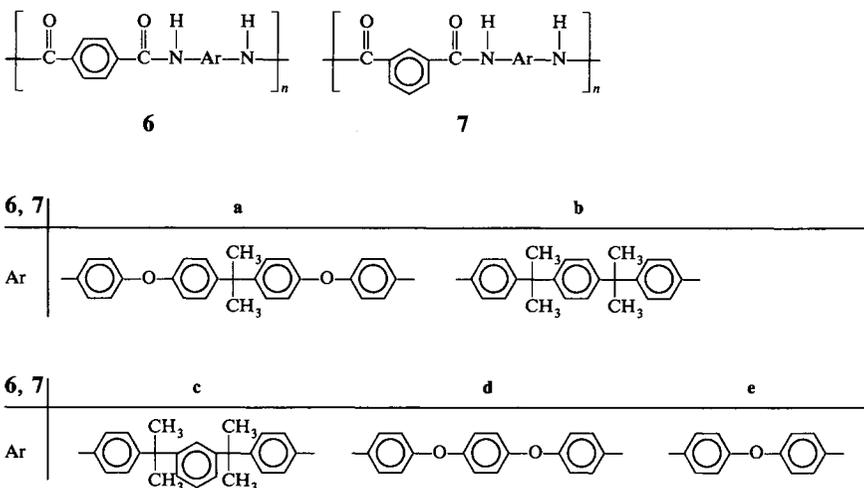
The thermal properties of all the polymers, as shown in Tab. 1, were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). All the glass transition temperatures ( $T_g$ 's) were recorded by the second heating DSC traces after quenching the samples from temperatures above  $T_g$  or  $T_m$ . Polymers *m*-5a, *m*-5d, *p*-5h, and *m*-5h showed melting endothermic peaks in the first heating DSC traces at 303 °C, 267 °C, 352 °C and 370 °C, respectively; the other polymers, however, showed no melting endotherms. Two neighboring endotherms at 326 °C and 352 °C were measurable in the first heating DSC trace of the polymer *p*-5h. Rapid quenching and subsequent analysis showed a clear glass transition at 230 °C and only one small endothermic peak around 325 °C, possibly due to the residual crystalline region. Polyamide *m*-5h also showed two endotherms around 326 and 370 °C in its first heating DSC trace. Rapid cooling and repeated heating showed only a  $T_g$  at 212 °C and disappearance of the melting transition. The DSC behavior indicated that the polyamides *p*- and *m*-5h as-polymerized exhibited crystallites of different size and slow rate of crystallization. The polyamides 5a–h from aromatic dicarboxylic acids had  $T_g$ 's in the range of 175–242 °C. There are 18–60 °C differences in  $T_g$  values between the *m*-isomeric and *p*-isomeric aromatic polyamides. The polyamides 5i–n, prepared from aliphatic dicarboxylic acids, showed relatively lower  $T_g$ 's, with *p*-isomers in the range of 130–160 °C and *m*-isomers ranging from 61–103 °C. In general,  $T_g$ 's were lowered with increasing length of methylene units for *p*-5i–n series polymers, whereas the decreasing order was disrupted in the *m*-5i–n series polymers. Poly(amide-imide)s *p*-5o–s had  $T_g$ 's between 182 and 245 °C, 25–42 °C higher than most of their corresponding *m*-isomers ( $T_g$  = 148–205 °C). Introduction of an aliphatic chain obviously decreased the  $T_g$  values.

From dynamic thermogravimetry, the temperatures at which 10% weight loss occurred in air or nitrogen and the residual wt.-% at 800 °C in nitrogen of all the obtained polymers were also summarized in Tab. 1. Almost all the polymers did not show significant weight loss up to 400 °C in air or nitrogen, and, in general, those

containing an aliphatic chain in the repeating unit displayed a lower decomposition temperature, leaving lower char yield when the polymers were heated to 800 °C in a nitrogen atmosphere.

For comparative purposes, two families of polyamides (**6a–e** and **7a–e**) were prepared by the condensation of terephthalic acid (TPA) and isophthalic acid (IPA) with some diamines containing ether and/or isopropylidene linkages between the phenylene units, such as 4,4'-[isopropylidenebis(1,4-phenyleneoxy)]dianiline, 4,4'-(1,4-phenylenediisopropylidene)dianiline, 4,4'-(1,3-phenylenediisopropylidene)dianiline, 4,4'-(1,4-phenylenedioxy)dianiline and 4,4'-oxydianiline (*Scheme 3*). The structure-property relationships of these polyamides, together with those of polymers *p-5a*,

*Scheme 3:*



*m-5a*, *p-5b*, and *m-5b*, were investigated. Some properties are shown in Tab. 2. The solubility of the polyamides was tested qualitatively in DMF, DMAc, and NMP. In the family of TPA-derived polyamides, the polymers **6d** and **6e**, which only contained ether connecting groups in the diamine moiety, were insoluble in these three solvents, and all other polyamides except for the polymer **6e** were dissolvable. This indicates that the isopropylidene linkage could impart better solubility to the polyamides than the ether group. On the other hand, the IPA-derived polyamides revealed higher solubility and could be readily dissolved in DMF, DMAc, or NMR except for polymer **7d** which was only partially soluble in DMF. The polyamides **6b**, **6d**, and **6e** could not be cast into films, because they were insoluble in organic solvents suitable for film-casting. All the other polyamides could be solution-cast into films in DMAc; however, the cast films of polymers *m-5a*, **6c**, and **7c** exhibited brittle characteristics, possibly due to a high degree of crystallization.

Tab. 2. Properties of polyterephthalamides and polyisophthalamides with different diamine moieties

Polymer	$\eta_{inh}^a)$ dL/g	Solubility <sup>b)</sup>		Film <sup>c)</sup> quality	$T_g^d)$ °C	$T_d^e)$ °C	Char yield <sup>f)</sup> in %
		DMF	DMAc or NMP				
<i>p</i> -5a	1,20	+	+	flexible	224	497	47,5
<i>m</i> -5a	0,73	+h	+	brittle	175	507	51,4
6a	3,33	+	+	flexible	— <sup>g)</sup>	503	60,2
6b	1,64	—	±	—	256	422	39,4
6c	0,79	+h	+	brittle	240	420	47,0
6d	2,09	—	—	—	—	532	61,0
6e	2,05	—	—	—	—	497	66,5
<i>p</i> -5a	0,89	+	+	flexible	217	493	44,8
<i>m</i> -5a	0,52	+	+	flexible	180	484	53,4
7a	1,15	+	+	flexible	227	493	55,1
7b	0,61	+	+	flexible	—	469	42,3
7c	0,79	+	+	brittle	—	423	53,3
7d	1,47	±	+	flexible	224	519	64,1
7e	0,91	+	+	flexible	280	506	66,9

a) Inherent viscosity measured at 30 °C with concentration of 0,5 g/dL in DMAc containing 5 wt.-% LiCl dissolved.

b) +: soluble at room temperature; ±: partially soluble; -: insoluble; +h: soluble on heating.

c) Polymer films were cast by slow evaporation of solution in DMAc.

d) Glass transition temperature defined as the centre point of the base line shift on the second DSC heating trace.

e) Temperature at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min in nitrogen.

f) Residual weight-% at 800 °C, in nitrogen.

g) Difficult to judge.

Polyamides **6d**, **6e**, **7d**, and **7e**, obtained from diamines containing the ether linker only, showed higher decomposition temperatures and higher char yields when heated to 800 °C in nitrogen than the corresponding polyamides **6b**, **6e**, **7b**, and **7c**, which contain only the isopropylidene connecting groups in the diamine moiety. These results indicate that incorporation of isopropylidene groups enhances solubility but diminishes thermal stability a little.  $T_g$ 's of the polyamides were high for short-chain diamine compositions and were lowered with increasing length of the diamine segment. In general, the higher the content of *m*-phenylene units in the polymer backbone, the lower the  $T_g$  values. Some polyamides showed no discernible base-line shifts in the DSC curves, so their  $T_g$  values were difficult to judge. Because the  $T_g$  data obtained are very limited, we cannot conclude whether the ether or isopropylidene group incorporated is more influential on the  $T_g$ 's of these polyamides.

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