

## Preparation and properties of poly(amide-imide)s derived from trimellitic anhydride, $\alpha$ -amino acids, and aromatic diamines<sup>a)</sup>

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### SUMMARY:

Four dicarboxylic acids containing one preformed imide ring were prepared by condensation of trimellitic anhydride with  $\alpha$ -amino acids such as glycine, DL-alanine, DL-valine, and DL-leucine. These diacids were subsequently directly polycondensated with various aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents in *N*-methyl-2-pyrrolidone (NMP) containing calcium chloride, producing various aliphatic-aromatic poly(amide-imide)s with pendant alkyl groups. The resultant polymers have inherent viscosities in the range of 0.58–2.15 dL/g and were amorphous, as revealed by wide-angle X-ray diffractograms. All polymers were readily soluble in a variety of solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and NMP, and could be cast from their DMAc solutions into transparent, flexible, and tough films. All poly(amide-imide)s showed clear glass transition temperatures in the range of 181–313 °C on the heating traces of differential scanning calorimetry (DSC). Almost all the poly(amide-imide)s exhibited no appreciable decomposition below 370 °C, with 10% weight loss being recorded above 400 °C in nitrogen and air. The polymers with larger side chain attached exhibited higher solubility, but lower glass transition temperature and initial decomposition temperature.

### Introduction

Polyimides are one of the most important class of thermally stable polymers, which are well known for their high-performance properties but have one major disadvantage of typically being insoluble and unprocessable after conversion from the poly(amic acid) to the polyimide form<sup>1,2</sup>. To overcome these problems, some copolymers have been proposed, in particular, poly(amide-imide)s, which can be linear, soluble, and also stable in contrast to poly(amic acid) solutions. This class of polymers seems to provide a favourable balance between processability and performance.

Various approaches have been carried out successfully in the synthesis of poly(amide-imide)s<sup>3–5</sup>. The triphenyl phosphite promoted polycondensation (or so-called Yamazaki phosphorylation-polyamidation) technique for the synthesis of polyamides has been reported by Yamazaki et al.<sup>6</sup> and has been extended to the synthesis of poly(amide-imide)s in our laboratory. This technique involves the direct polycondensation of aromatic amino acids or aromatic diamines with aromatic or aliphatic dicar-

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boxylic acids in a medium consisting of *N*-methyl-2-pyrrolidone (NMP) containing dissolved inorganic salts in the presence of an aryl phosphite and an organic base. In general, as long as the resulting polymers do not precipitate in the Yamazaki reaction medium, high-molecular-weight poly(amide-imide)s can be obtained by the phosphorylation reaction from dicarboxylic acids having preformed imide rings and aromatic diamines. In our previous studies<sup>7-10</sup> we have successfully applied the Yamazaki phosphorylation to the synthesis of high-molecular-weight poly(amide-imide)s from aromatic diamines and several imide ring-containing dicarboxylic acids. This route has been proved to be more convenient and efficient when compared with the imide-containing diacid chloride method<sup>11</sup>. Various combinations of amino acids and trimellitic anhydride or aromatic tetracarboxylic dianhydrides as well as the combination of diamines (aliphatic or aromatic) with trimellitic anhydride give a number of imide ring-containing diacids, which can be used as poly(amide-imide) building blocks. Thus, many structurally new poly(amide-imide)s can be easily produced by the direct polycondensation route.

$\alpha$ -Amino acids are the main constituents of many naturally occurring compounds, such as proteins or polypeptides. For example, silk is a protein in which almost one-half of the polypeptide chain is derived from the simplest amino acid, glycine ( $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ ), and half of the remainder is derived from alanine [ $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{COOH}$ ]. Many other  $\alpha$ -amino acids occur in the free state in plant or animal tissue. Researches concerning  $\alpha$ -amino acids have added major emphasis to the biological area, e.g., the use of biologically active peptides and small proteins, tissue and cell culture applications, and preparation of molecular biology products, etc. Amino acids can be obtained by hydrolysis of a protein; or they can be synthesized in various ways, specially by fermentation of glucose. Therefore, it may be possible to employ amino acids as a cheap raw material for the synthesis of polymers in addition to polypeptides. To our knowledge,  $\alpha$ -amino acid moieties are scarcely incorporated into the backbones of polymers other than polypeptides. In continuation of our study on new poly(amide-imide) syntheses<sup>12-14</sup>, we report here the successful results of introducing some  $\alpha$ -amino acid moieties into the polymer backbone of poly(amide-imide)s that comprize as further constituents trimellitic anhydride and an aromatic diamine.

## Experimental part

### Materials

Trimellitic anhydride (TMA) (from Wako) was used without previous purification. Four  $\alpha$ -amino acids, i.e., glycine (TCI), DL-alanine (DL-2-aminopropionic acid) (Sigma), DL-valine (DL-2-amino-3-methylbutanoic acid) (Sigma), and DL-leucine (DL-2-amino-4-methylpentanoic acid) (Sigma), were also 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. *p*-Phenylenediamine was vacuum distilled prior to use. All other aromatic diamines were of high purity when received from the manufacturers and used without any further purification.

*Synthesis of imide-diacids*

Imide-dicarboxylic acids 2-1 to 2-4 were synthesized by condensation of trimellitic anhydride with  $\alpha$ -amino acids,  $H_2N-CRH-COOH$ , containing different alkyl group,  $R = H, CH_3, CH(CH_3)_2$ , and  $CH_2CH(CH_3)_2$ . As an example, we describe the preparation of 2-2, corresponding to  $R = CH_3$  for DL-alanine.

*2-(4-Carboxyphthalimido)propionic acid (2-2)*: 19,2 g (0,1 mol) of trimellitic anhydride and 8,9 g (0,1 mol) of DL-alanine were dissolved in 100 mL of dried DMF. The stirred reaction mixture was first heated at 60 °C for 1 h. Then, 50 mL of toluene was added, and the mixture was heated at reflux until about 1,8 mL of water was distilled azeotropically. On cooling, after acidification with a 30% aqueous HCl solution, a white product precipitated and was separated from the final reaction solution. The crude product was recrystallized from DMF/water to give granular crystals; m. p. 265 °C. Yield: 23 g (87,5%).

IR (KBr): 2500–3500  $cm^{-1}$  (carboxylic, —OH), 1715  $cm^{-1}$  (carboxylic, C=O), 1783 and 1730  $cm^{-1}$  (imide, C=O), 733  $cm^{-1}$  (imide ring).

$C_{12}H_9NO_6$ (263,20)	Calc.	C 54,76	H 3,45	N 5,32
	Found	C 54,74	H 3,54	N 5,20

The other imide-diacids were synthesized in a similar manner.

*4-Carboxyphthalimidoacetic acid (2-1)*: m. p. 268 °C, yield 84,0%.

$C_{11}H_7NO_6$ (249,17)	Calc.	C 53,02	H 2,83	N 5,62
	Found	C 53,02	H 2,59	N 5,57

*2-(4-Carboxyphthalimido)-3-methylbutanoic acid (2-3)*: m. p. 209 °C, yield 81,9%.

$C_{12}H_9NO_6$ (263,20)	Calc.	C 57,73	H 4,50	N 4,81
	Found	C 57,69	H 4,54	N 4,64

*2-(4-Carboxyphthalimido)-4-methylpentanoic acid (2-4)*: m. p. 231 °C, yield 82,3%.

$C_{15}H_{15}NO_6$ (263,20)	Calc.	C 59,01	H 4,95	N 4,59
	Found	C 58,88	H 5,00	N 4,44

*Polycondensation*

A typical example of polycondensation was as follows: A mixture of 0,66 g (2,5 mmol) of diacid 2-2, 0,27 g (2,5 mmol) of *p*-phenylenediamine (3a), 0,8 g of calcium chloride, 1,6 mL of TPP, 1,5 mL of pyridine, and 5 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 500 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, and the inherent viscosity of the polymer in DMAc containing 5 wt.-% LiCl was 1,18 dL/g, measured at a concentration of 0,5 g/dL at 30 °C.

$(C_{18}H_{13}N_3O_4)_n$ (335,30) <sub>n</sub>	Calc.	C 64,47	H 3,91	N 12,53
	Found	C 64,53	H 3,97	N 12,46

IR (film): 3300, 1670, and 1560  $cm^{-1}$  (amide), 1780 and 1720  $cm^{-1}$  (imide ring, symmetrical and asymmetrical C=O stretching), 725  $cm^{-1}$  (imide ring deformation).

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

### Measurements

The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30 °C. Weight-average molecular weight ( $\overline{M}_w$ ) and number-average molecular weight ( $\overline{M}_n$ ) 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). Elemental analyses were run in a Perkin-Elmer Model 240 C, H, N analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained with a Jeol EX-400 NMR spectrometer, 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 a rate of 20 °C/min in flowing nitrogen (30 cm<sup>3</sup>/min). Thermomechanical analysis (TMA) was performed with a Rigaku thermoflex TMA 8140 (penetration method) coupled to a Rigaku TAS-100 thermal analysis station. Thermogravimetry (TG) was done on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100. Experiments were performed with  $10 \pm 2$  mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min.

The wide-angle X-ray scattering measurements were performed at room temperature (about 25 °C) on film specimens of about 0,1 mm thickness on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered  $\text{CuK}\alpha$  radiation (operating at 40 kV and 15 mA). The intensity, measured at a scanning rate of 2°/min, was recorded for the angular range 5–40° ( $2\theta$ ).

Tensile measurements were performed at room temperature (ca. 20 °C) for all films on an Instron Universal Tester Model 1130. Film dimensions were 0,5 × 6 cm, about 0,1 mm thick. Data of an average of at least five individual determinations were used.

### Results and discussion

#### Synthesis of imide-diacid monomers

The imide ring-containing diacids **2-1** to **2-4** (Fig. 1) were synthesized from the corresponding  $\alpha$ -amino acids and trimellitic anhydride (Scheme 1). Complete cyclization

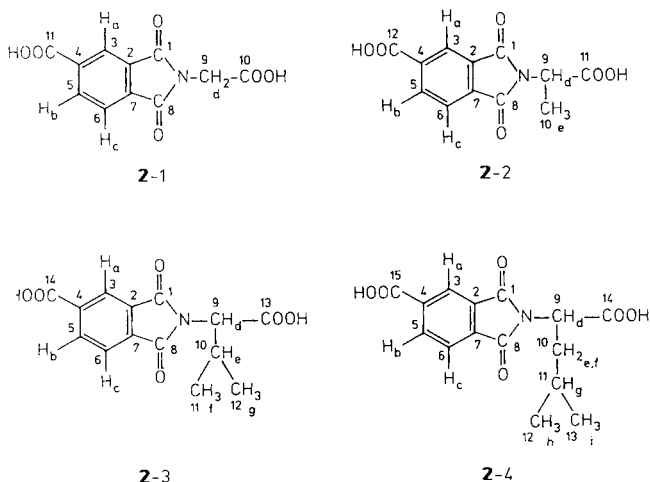
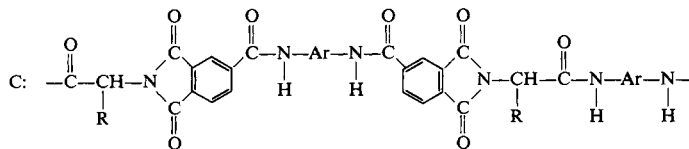
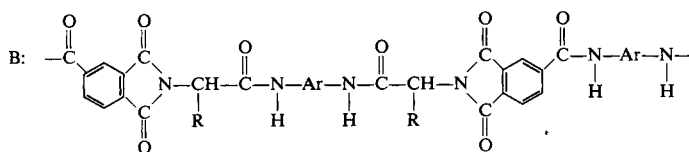
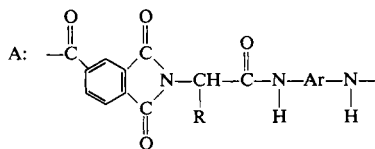
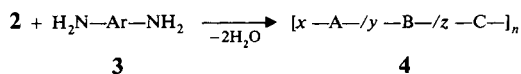
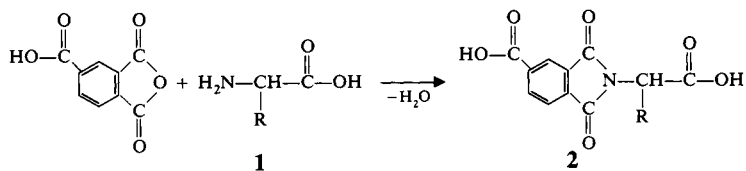


Fig. 1. Imide-dicarboxylic acids **2-1** to **2-4** with notation for NMR assignment (s. Fig. 2)

Scheme 1:



	1, 2, 4-1	-2	-3	-4
R	H	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>

	3, 4a	b	c
Ar			

	d	e

	f	g

of the intermediate amic acid was achieved by toluene-water azeotropic distillation. The yields of these imide-diacids were high, and their elemental analyses and characteristic IR absorptions agree well with the proposed structures.

The structure of imide-diacids was also confirmed by NMR spectra. Numbered formula of imide-diacids appear in Fig. 1. Fig. 2 shows the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR

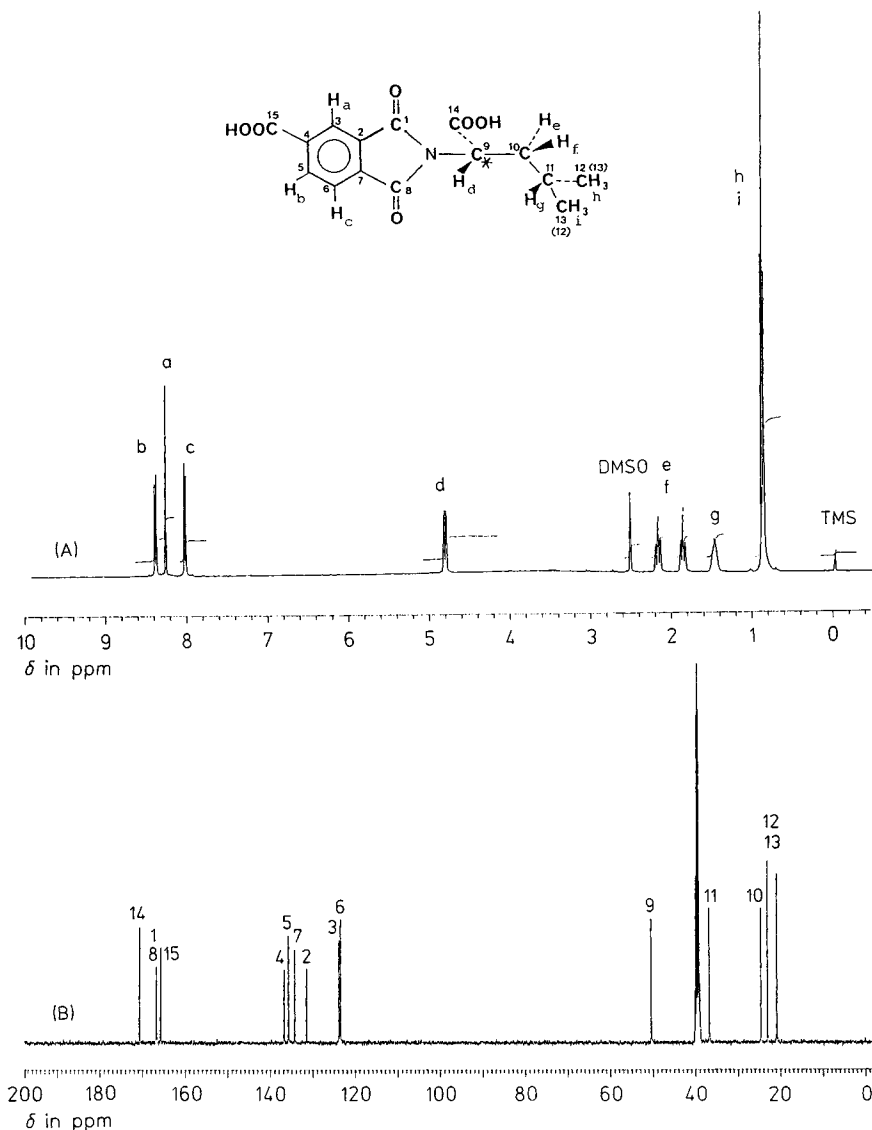


Fig. 2.  $^1\text{H}$  NMR (A) and  $^{13}\text{C}$  NMR (B) spectra of imide-diacid 2-4 in  $\text{DMSO}-d_6$

spectra of the representative imide-diacid 2-4 and the assignments of all carbons and protons. All expected absorptions are observed.

In  $^1\text{H}$  NMR spectrum [Fig. 2(A)], the absorption signals of aromatic protons appear in the range of  $\delta$  8,02–8,38 ppm. The chemical shifts of the diastereomeric (diastereotropic) methylene protons,  $\text{H}_e$  and  $\text{H}_f$ , are quite different. Thus, the  $n + 1$  pattern is not observed, but instead, a more complicated splitting pattern emerges. The methine proton  $\text{H}_d$  reveals two close doublets centred at about 4,80 ppm due to the presence of magnetically nonequivalent  $\text{H}_e$  and  $\text{H}_f$ . In addition to geminal coupling between  $\text{H}_e$  and  $\text{H}_f$ , each of them is coupled by  $\text{H}_d$  and  $\text{H}_g$  simultaneously; therefore, the result of signal splitting gives two groups of multiplet around 2,16 and 1,85 ppm. Besides, the two methyl groups of 2-4 also show splitting due to diastereomers. The methyl protons give very close doublets and appear together like a triplet at 0,85 ppm.

In the  $^{13}\text{C}$  NMR spectrum, most carbon atoms gave separate and assignable resonances. In the carbonyl region, the aliphatic carboxylic acid appears at 170,7 ppm,

Tab. 1. Proton and carbon-13 chemical shifts<sup>a)</sup> ( $\delta$  in ppm) as well as assignments of imide-dicarboxylic acids

Assignment <sup>b)</sup>	2-1	2-2	2-3	2-4
$\text{C}^1$	166,5	166,4	166,8	166,7
$\text{C}^2$	131,9	131,7	131,4	131,5
$\text{C}^3$	123,9	123,8	123,9	123,9
$\text{C}^4$	136,7	136,6	136,8	136,8
$\text{C}^5$	135,8	135,6	135,8	135,8
$\text{C}^6$	123,5	123,4	123,6	123,5
$\text{C}^7$	134,7	134,6	134,2	134,3
$\text{C}^8$	166,5	166,4	166,8	166,7
$\text{C}^9$	39,5	47,3	57,3	50,5
$\text{C}^{10}$	168,8	14,8	28,1	24,6
$\text{C}^{11}$	165,8	170,9	20,8	36,8
$\text{C}^{12}$		165,8	19,2	23,0
$\text{C}^{13}$			169,6	20,9
$\text{C}^{14}$			165,7	170,7
$\text{C}^{15}$				165,8
$\text{H}^a$	8,28 (s) <sup>c)</sup>	8,27 (s)	8,30 (s)	8,26 (s)
$\text{H}^b$	8,39 (d)	8,39 (d)	8,43 (d)	8,38 (d)
$\text{H}^c$	8,04 (d)	8,03 (d)	8,06 (d)	8,02 (d)
$\text{H}^d$	4,36 (s)	4,92 (q)	4,52 (d)	4,80 (d)
$\text{H}^e$		1,58 (d)	2,61 (m)	2,16 (m)
$\text{H}^f$				1,85 (m)
$\text{H}^g$			1,10 (d)	1,46 (m)
$\text{H}^h$			0,87 (d)	0,85 (d)
$\text{H}^i$				0,86 (d)

a) Internal reference  $\text{DMSO-}d_6$  ( $\delta = 39,50$  ppm) for  $^{13}\text{C}$  NMR spectra; external reference TMS ( $\delta = 0,00$  ppm) for  $^1\text{H}$  NMR spectra.

b) Atoms numbered according to Fig. 1.

c) s: singlet; d: doublet; q: quartet; m: multiplet.

Tab. 2. Synthesis of poly(amide-imide)s<sup>a)</sup>

Polymer	$\eta_{inh}^{b)}$ dL/g	$10^{-4} \cdot \overline{M}_w^{c)}$	$10^{-4} \cdot \overline{M}_n^{c)}$	$\overline{M}_w/\overline{M}_n$
4a-1	1,78	21,3	8,4	2,54
4b-1	2,15	23,2	9,0	2,58
4c-1	1,57	15,0	7,1	2,11
4d-1	1,37	16,7	6,3	2,65
4e-1	1,67	19,2	8,0	2,40
4f-1	2,14	29,6	11,0	2,69
4g-1	1,52	21,1	9,2	2,29
4a-2	1,18	8,7	3,6	2,44
4b-2	1,18	10,6	4,7	2,26
4c-2	1,23	12,2	4,9	2,49
4d-2	1,12	8,1	3,5	2,31
4e-2	1,15	9,7	4,0	2,42
4f-2	1,34	13,1	5,5	2,28
4g-2	1,14	10,2	4,2	2,43
4a-3	0,75	5,2	2,7	1,93
4b-3	0,82	7,0	3,2	2,18
4c-3	0,58	5,0	2,5	2,00
4d-3	0,72	6,2	2,9	2,14
4e-3	0,64	5,9	2,9	2,03
4f-3	1,04	9,8	4,2	2,33
4g-3	0,88	8,2	3,8	2,16
4a-4	1,07	7,9	3,4	2,32
4b-4	1,03	8,0	3,5	2,28
4c-4	0,82	6,9	3,1	2,22
4d-4	0,71	5,4	2,7	2,00
4e-4	0,82	8,9	3,8	2,34
4f-4	1,23	14,2	5,9	2,41
4g-4	1,21	14,6	6,0	2,43

a) Polymerization was carried out with 2,5 mmol of each monomer, 1,6 mL of TPP, 1,5 mL of pyridine, and 0,8 g of CaCl<sub>2</sub> in 5 mL of NMP, at 105 °C, for 3 h, under nitrogen.

b) Measured at a concentration of 0,5 g/dL in DMAc containing 5 wt.-% of LiCl dissolved, at 30 °C.

c) Determined by GPC.

the aromatic carboxylic acid at 165,8 ppm and the phthalimide group gives one signal (coinciding accidentally) at 166,7 ppm. Six resonance peaks in the range of 123,5–136,8 ppm are peculiar to the aromatic carbons. In the aliphatic region, the finding that the signals of methyl carbon are doubled is of specific interest. This can be attributed to the existence of a chiral center at the adjacent carbon atom (C<sub>9</sub>).

The proton and carbon-13 chemical shifts of all imide-diacids are summarized in Tab. 1. The carbon assignment was made with the help of the nuclear Overhauser effect (NOE) in <sup>13</sup>C NMR spectroscopy, together with measurements of proton-coupled <sup>13</sup>C NMR spectra.



## Polymer synthesis

Direct polycondensation of aromatic diamines with dicarboxylic acids using triphenyl phosphite and pyridine as the condensing agents has been known to be a convenient method for the preparation of aromatic polyamides on a laboratory scale<sup>6</sup>. Four series of poly(amide-imide)s **4(a-g)-1**, **4(a-g)-2**, **4(a-g)-3**, and **4(a-g)-4** with different pendant groups were prepared from the imide-dicarboxylic acids **2-1** to **2-4** and various diamines **3a-g** by using this direct polycondensation technique (*Scheme 1*). Yet, owing to the asymmetry of the diacids **2-1** to **2-4**, these poly(amide-imide)s may contain different mole fractions and sequences of the repeating units A, B, and C. Because the synthesis of the poly(amide-imide)s is carried out at a moderately high

Tab. 3. Elemental analyses of poly(amide-imide)s

Polymer	Formula (Mol. weight)	Elemental analysis					
		Calc.			Found		
		C	H	N	C	H	N
<b>4a-1</b>	(C <sub>17</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (321,29) <sub>n</sub>	63,55	3,45	13,08	62,93	3,50	12,98
<b>4b-1</b>	(C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (413,39) <sub>n</sub>	66,83	3,66	10,16	65,50	3,73	10,22
<b>4c-1</b>	(C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (413,39) <sub>n</sub>	66,83	3,66	10,16	65,60	3,75	10,01
<b>4d-1</b>	(C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (411,42) <sub>n</sub>	70,06	4,16	10,21	69,50	4,23	9,98
<b>4e-1</b>	(C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub> (429,45) <sub>n</sub>	64,33	3,52	9,78	63,10	3,78	9,10
<b>4f-1</b>	(C <sub>29</sub> H <sub>19</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (508,48) <sub>n</sub>	68,50	3,77	8,26	67,20	3,93	7,86
<b>4g-1</b>	(C <sub>29</sub> H <sub>19</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (508,48) <sub>n</sub>	68,50	3,77	8,26	67,10	3,85	7,93
<b>4a-2</b>	(C <sub>18</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (335,32) <sub>n</sub>	64,47	3,91	12,53	64,53	3,97	12,46
<b>4b-2</b>	(C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (427,41) <sub>n</sub>	67,44	4,01	9,83	67,40	4,13	9,58
<b>4c-2</b>	(C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (427,41) <sub>n</sub>	67,44	4,01	9,83	67,00	4,10	9,10
<b>4d-2</b>	(C <sub>25</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (425,44) <sub>n</sub>	70,58	4,50	9,88	69,85	4,63	9,53
<b>4e-2</b>	(C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub> (433,48) <sub>n</sub>	65,00	3,86	9,47	64,53	3,98	9,12
<b>4f-2</b>	(C <sub>30</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (519,51) <sub>n</sub>	69,36	4,07	8,09	68,85	4,23	8,01
<b>4g-2</b>	(C <sub>30</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (519,51) <sub>n</sub>	69,36	4,07	8,09	68,57	4,21	7,95
<b>4a-3</b>	(C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (363,37) <sub>n</sub>	66,11	4,71	11,56	65,90	4,79	10,99
<b>4b-3</b>	(C <sub>26</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (455,47) <sub>n</sub>	68,56	4,65	9,22	68,10	4,70	9,10
<b>4c-3</b>	(C <sub>26</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (455,47) <sub>n</sub>	68,56	4,65	9,22	68,02	4,68	9,15
<b>4d-3</b>	(C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (453,50) <sub>n</sub>	71,51	5,11	9,26	70,88	5,13	9,20
<b>4e-3</b>	(C <sub>26</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub> (471,53) <sub>n</sub>	66,23	4,99	8,91	64,85	5,03	8,70
<b>4f-3</b>	(C <sub>32</sub> H <sub>25</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (547,57) <sub>n</sub>	70,19	4,60	7,67	69,50	4,83	7,45
<b>4g-3</b>	(C <sub>32</sub> H <sub>25</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (547,57) <sub>n</sub>	70,19	4,60	7,67	69,63	4,90	7,23
<b>4a-4</b>	(C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (377,40) <sub>n</sub>	66,83	5,07	11,13	66,23	4,98	11,01
<b>4b-4</b>	(C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (469,49) <sub>n</sub>	69,07	4,94	8,95	69,01	4,95	8,97
<b>4c-4</b>	(C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub> ) <sub>n</sub> (469,49) <sub>n</sub>	69,07	4,94	8,95	69,01	4,98	8,90
<b>4d-4</b>	(C <sub>28</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>n</sub> (467,52) <sub>n</sub>	71,93	5,39	8,99	71,80	5,30	8,83
<b>4e-4</b>	(C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub> (485,56) <sub>n</sub>	66,79	4,77	8,65	66,22	4,80	8,59
<b>4f-4</b>	(C <sub>33</sub> H <sub>27</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (561,59) <sub>n</sub>	70,58	4,84	7,48	70,43	4,89	7,10
<b>4g-4</b>	(C <sub>33</sub> H <sub>27</sub> N <sub>3</sub> O <sub>6</sub> ) <sub>n</sub> (561,59) <sub>n</sub>	70,58	4,84	7,48	69,88	4,93	7,32

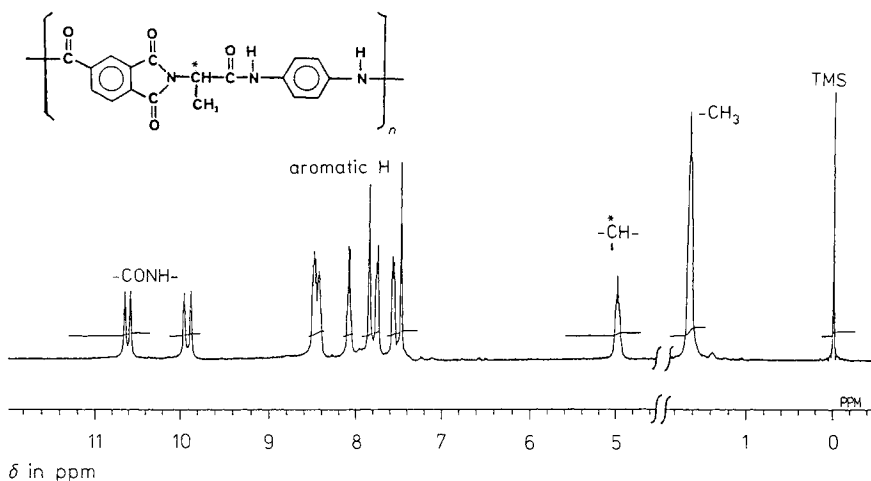


Fig. 3. <sup>1</sup>H NMR spectrum of poly(amide-imide) 4a-2 in DMSO-*d*<sub>6</sub>

temperature (about 105 °C), incorporation of nearly equal amounts of units A, B, and C with nearly random sequence is highly probable.

Tab. 2 summarizes the results of the polymerization. Almost all the reactions proceeded readily in homogeneous solution, and gave quantitative yields of poly-(amide-imide)s with moderate to high inherent viscosities in the range of 0.58–2.15 dL/g in DMAc/5 wt.-% LiCl. The GPC curves indicated that the  $\bar{M}_w$  values of poly-(amide-imide)s were in the range of 50 000–297 000 relative to standard polystyrene, and the  $\bar{M}_w/\bar{M}_n$  values, a measure of the molecular weight distribution, were not too broad (1.93–2.70). It can be deduced from the inherent viscosities (or the molecular weights) of the resultant poly(amide-imide)s that the alkyl group of the imide-diacids exerted an unfavorable effect on the propagation of polymer chain, possibly due to steric hindrance. In particular, the isopropyl group of imide-diacid 2-3 showed the most serious effect. Nevertheless, the molecular weights of all the poly(amide-imide)s, including the 4-3 series, are sufficiently high to permit casting of tough films.

The formation of poly(amide-imide)s was confirmed by elemental analysis and IR and NMR spectroscopy. The elemental analysis values of these poly(amide-imide)s were in good agreement with the values calculated for the proposed structures (Tab. 3).

The IR spectra of the polymers showed characteristic amide absorptions near 3300  $\text{cm}^{-1}$  (N—H) and 1670  $\text{cm}^{-1}$  (C=O), together with characteristic imide absorptions near 1780  $\text{cm}^{-1}$  (asym. C=O stretching of imide ring), 1720  $\text{cm}^{-1}$  (sym. C=O stretching of imide ring), and 725  $\text{cm}^{-1}$  (imide ring deformation). Fig. 3 shows the <sup>1</sup>H NMR spectrum of polymer 4a-2 as a typical example. Peaks at 10.57 and 9.42 ppm correspond, respectively, to NH resonances from aromatic and aliphatic amides. The doublet pattern indicates that protons on the amide linkage are sensitive to mixed substitutions of the type aliphatic-aliphatic, aliphatic-aromatic, and aromatic-aromatic (see *Scheme 1*). The same intensity of the NH resonances suggests a statistical random distribution of A, B, and C segments in the polymer.

*Properties of polymers*

The qualitative solubility of poly(amide-imide)s in various solvents is shown in Tab. 4. All poly(amide-imide)s were readily soluble in polar solvents such as DMAc, DMF, NMP, DMSO, and *m*-cresol. Except for those derived from *p*-phenylenediamine, polymers with bulky alkyl pendant group were also soluble in tetrahydrofuran (THF). The high solubility can be apparently attributed to the introduction of pendant alkyl group and to the use of asymmetrical trimellitimide in the polymer backbone. All the polymers are practically insoluble in common organic solvents, such as benzene, acetone, chloroform, etc.

Tab. 4. Solubility of poly(amide-imide)s<sup>a)</sup>

Polymer	Solvents <sup>b)</sup>					
	DMAc	DMF	NMP	DMSO	<i>m</i> -cresol	THF
4a-1	+	+	+	+	-	-
4b-1	+	+	+	+	+	-
4c-1	+	+	+	+	+	-
4d-1	+	+	+	+	+	-
4e-1	+	+	+	+	+	-
4f-1	+	+	+	+	+	-
4g-1	+	+	+	+	+	-
4a-2	+	+	+	+	+	-
4b-2	+	+	+	+	+	-
4c-2	+	+	+	+	+	-
4d-2	+	+	+	+	+	-
4e-2	+	+	+	+	+	-
4f-2	+	+	+	+	+	-
4g-2	+	+	+	+	+	-
4a-3	+	+	+	+	+	-
4b-3	+	+	+	+	+	+
4c-3	+	+	+	+	+	+
4d-3	+	+	+	+	+	+
4e-3	+	+	+	+	+	+
4f-3	+	+	+	+	+	+
4g-3	+	+	+	+	+	+
4a-4	+	+	+	+	+	-
4b-4	+	+	+	+	+	+
4c-4	+	+	+	+	+	+
4d-4	+	+	+	+	+	+
4e-4	+	+	+	+	+	+
4f-4	+	+	+	+	+	+
4g-4	+	+	+	+	+	+

<sup>a)</sup> +: soluble at room temperature; -: insoluble.

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

X-ray diffraction studies indicated that all the poly(amide-imide)s were amorphous. Transparent, flexible, and tough films could be cast from the DMAc solutions of all the poly(amide-imide)s. The tensile properties of the polymer films are summarized in Tab. 5. The films had tensile strengths of 44–90 MPa, elongations at break of 5–56%, and initial moduli of 1,78–2,67 GPa. Some poly(amide-imide)s containing glycine or alanine moiety, such as **4a-1**, **4b-1**, **4c-1**, **4f-2**, and **4g-2**, behaved as ductile materials; they yield during tension and were more elongated. In most cases, incorporation of bulky pendant alkyl groups caused the disappearance of the yield point and a decrease in the elongation at break, especially for polymers with low molecular weights. This phenomenon may be explained by the fact that the presence of the bulky side group hinders the alignment of polymer chains under tension.

The thermal behavior of the polymers was characterized by means of differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermogravi-

Tab. 5. Tensile properties of poly(amide-imide) films

Polymer	Strength at yield in MPa	Strength at break in MPa	Elongation at break in %	Initial modulus in GPa
<b>4a-1</b>	85	82	46	2,46
<b>4b-1</b>	80	68	56	1,94
<b>4c-1</b>	87	70	40	2,10
<b>4d-1</b>	89	77	10	2,49
<b>4e-1</b>	77	65	13	1,80
<b>4f-1</b>	99	90	32	2,67
<b>4g-1</b>	80	72	9	2,06
<b>4a-2</b>	80	68	7	2,16
<b>4b-2</b>	80	72	9	2,11
<b>4c-2</b>	77	44	7	2,01
<b>4d-2</b>	71	64	23	1,96
<b>4e-2</b>	71	61	16	1,90
<b>4f-2</b>	72	63	40	1,83
<b>4g-2</b>	67	50	34	1,78
<b>4a-3</b>	—	45	5	2,10
<b>4b-3</b>	78	74	8	2,11
<b>4c-3</b>	—	71	5	2,01
<b>4d-3</b>	—	74	7	1,88
<b>4e-3</b>	—	76	8	1,98
<b>4f-3</b>	80	68	18	1,84
<b>4g-3</b>	—	72	6	2,05
<b>4a-4</b>	80	73	12	2,19
<b>4b-4</b>	—	70	8	1,89
<b>4c-4</b>	—	72	5	2,05
<b>4d-4</b>	76	73	9	1,89
<b>4e-4</b>	—	71	7	1,96
<b>4f-4</b>	86	78	19	1,89
<b>4g-4</b>	80	70	17	1,85

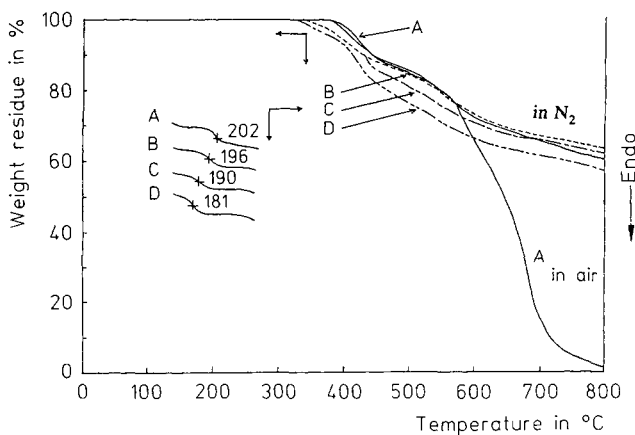


Fig. 4. TG and the second DSC heating traces (at a heating rate of 20 °C/min) of the series of poly(amide-imide)s **4g-1** to **4g-4**. (A): **4g-1** (R = H), (B): **4g-2** (R = CH<sub>3</sub>), (C): **4g-3** (R = CH(CH<sub>3</sub>)<sub>2</sub>), (D): **4g-4** (R = CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>)

metry (TG). Fig. 4 shows typical DSC and TG curves of poly(amide-imide)s **4g**. Polymer **4g-1** showed a very similar TG behavior in both nitrogen and air below 550 °C, but when the temperature was raised above 550 °C, the polymer showed a rapid weight loss and decomposed nearly completely at 800 °C in air. As can be seen from Fig. 4, the presence of alkyl side chains led to an earlier decomposition, due to the less thermally stable nature of aliphatic groups. The introduction of alkyl side chains also caused a decrease in glass transition temperatures ( $T_g$ ). This is reasonable because poly(amide-imide)s based on amino acids with bulky alkyl groups suffer strong steric interference between the alkyl groups, which forces the polymer chains apart from one another and so disrupts the hydrogen bonds.

The thermal data of all poly(amide-imide)s are summarized in Tab. 6. These polymers lost 10% weight at temperatures in the range of 393–457 °C in nitrogen and 387–432 °C in air, and left 50.2–62.1% char residue at 800 °C in nitrogen. The presence of the aliphatic side chain led to a lower initial decomposition temperature. The series of poly(amide-imide)s **4(a–g)-1** evidently showed high initial decomposition temperature because of the lack of the pendant alkyl group.

In all cases  $T_g$ 's of these polymers could be easily determined from the second heating traces of DSC after quenching the samples from elevated temperatures. In general, incorporation of a pendant alkyl group leads to a decrease of  $T_g$ , and the order of lowering effect is: isobutyl > isopropyl > methyl group. For the series of poly(amide-imide)s derived from the same imide-diacid, that from *p*-phenylenediamine exhibited the highest  $T_g$ , and incorporation of kinks between aromatic rings, such as oxygen bridge or *meta* catenation, lowered  $T_g$ . Furthermore, the softening temperature (which may be considered as apparent  $T_g$ ) of polymer films measured by TMA showed a similar decreasing tendency as  $T_g$  generated by DSC, although the values were much lower than  $T_g$ 's. This difference may be explained by the fact that these alkylene-containing poly(amide-imide)s exhibit a high degree of plasticity near  $T_g$ .

Tab. 6. Thermal properties of poly(amide-imide)s

Polymer	$T_g/^\circ\text{C}^{\text{a}}$	$T_s/^\circ\text{C}^{\text{b}}$	$T_d/^\circ\text{C}^{\text{c}}$		Residual wt.-% at 800 °C in N <sub>2</sub>
			in air	in N <sub>2</sub>	
4a-1	313	203	449	456	50,2
4b-1	261	205	440	441	56,0
4c-1	256	164	437	442	54,6
4d-1	261	156	456	457	58,1
4e-1	271	163	451	454	56,4
4f-1	249	141	419	422	56,1
4g-1	202	144	432	435	59,2
4a-2	275	206	392	405	59,2
4b-2	240	175	404	412	60,1
4c-2	221	150	400	406	61,6
4d-2	234	165	418	407	61,7
4e-2	225	157	401	406	60,0
4f-2	211	146	419	417	58,3
4g-2	196	124	414	417	62,1
4a-3	248	180	387	393	60,2
4b-3	218	167	394	402	61,0
4c-3	200	143	402	394	60,4
4d-3	219	162	414	408	60,0
4e-3	217	161	406	409	57,4
4f-3	209	137	408	415	59,7
4g-3	190	146	414	416	61,2
4a-4	242	191	390	399	54,1
4b-4	212	157	393	397	56,8
4c-4	194	139	388	399	59,1
4d-4	201	150	396	398	57,2
4e-4	215	167	393	399	54,3
4f-4	206	157	399	403	54,0
4g-4	181	136	404	406	56,4

a) From the second heating traces of DSC measurements conducted at a heating rate of 20 °C/min in nitrogen.

b) Softening point was determined by TMA with a load 10 g at a heating rate of 10 °C/min.

c) Decomposition temperature at which 10% weight loss was recorded with thermogravimetry (TG) at a heating rate of 20 °C/min.

## Conclusion

Moderate to high-molecular-weight poly(amide-imide)s containing  $\alpha$ -amino acid residues could be easily prepared from the phosphorylation-polyamidation reaction of aromatic diamines with imide ring-containing dicarboxylic acids obtained from trimellitic anhydride and  $\alpha$ -amino acids. All the poly(amide-imide)s showed an amorphous nature, as revealed by X-ray diffractograms, and could be solution cast into transparent, flexible, and tough films. Existence of pendant alkyl groups lowered the  $T_g$  values and the thermal stability of polymers.

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