

## Preparation of poly(amide-imide)s by means of triphenyl phosphite, 1

### Aliphatic-aromatic poly(amide-imide)s based on trimellitimide

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#### SUMMARY:

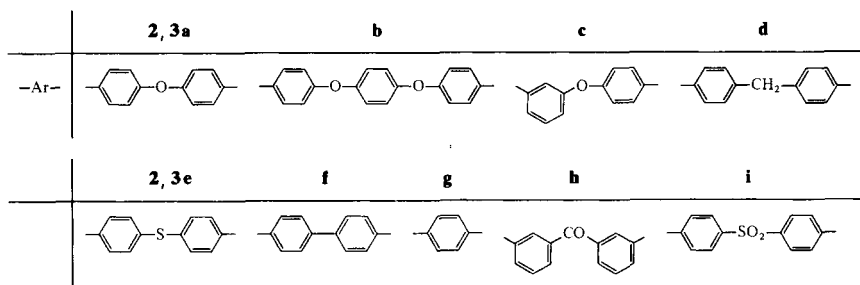
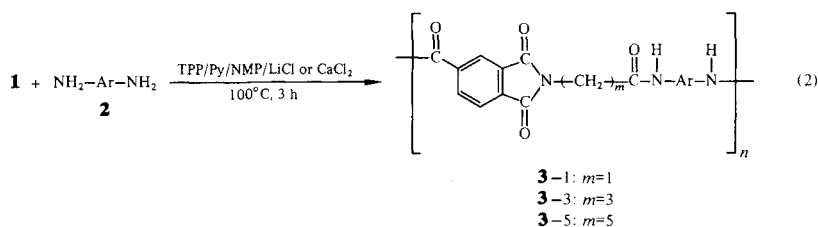
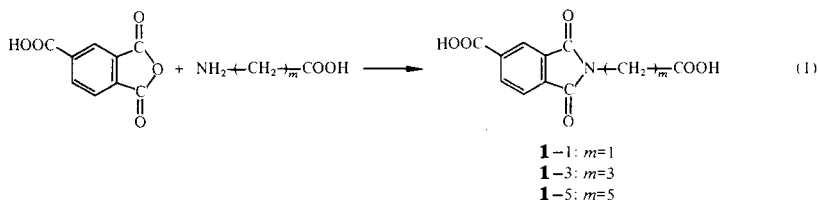
Aliphatic-aromatic poly(amide-imide)s with high molecular weight ( $\eta_{inh}$  up to 2,91 dl/g in DMAc/5% LiCl) were synthesized by direct polycondensation reaction of imide-containing dicarboxylic acids and aromatic diamines using triphenyl phosphite in *N*-methyl-2-pyrrolidone (NMP)/pyridine solution in the presence of metal salts. The factors affecting the reaction of *N*-(trimellitoyl)glycine and 4,4'-oxydianiline were investigated. The molecular weight of the polymer varied with the amount of metal salts, showing a maximum at a concentration of about 1 wt.-%  $CaCl_2$  or about 2 wt.-% LiCl in the reaction mixture. A monomer concentration of about 0,2 mol/l gave the most favorable result. Among the solvents tested, NMP was most effective. Similarly, polycondensations of several combinations of three imide-diacids with various aromatic diamines were carried out. Solubility, thermal properties, and tensile properties of the polymers are discussed.

#### Introduction

Poly(amide-imide)s are well-known to be thermally stable polymers. These polymers are usually prepared through poly(amic acid) intermediates, followed by thermal or chemical cyclization to form imide rings. Poly(amic acid)s are hydrolytically unstable and require special storage and handling care. Wrasidlo and Augl<sup>1)</sup> prepared poly(amide-imide)s from monomers with preformed imide rings. These monomers are favorable for preparing soluble and high-molecular-weight poly(amide-imide)s. The synthesis and characterization of aliphatic-aromatic poly(amide-imide)s from diamines and imide groups containing diacid chlorides have been reported by Abajo et al.<sup>2)</sup> They also studied the polycondensation reaction between a diisocyanate and an imide-containing diacid and established the factors affecting molecular weight and polymer structure<sup>3,4)</sup>.

The reaction with triphenyl phosphite has been found to be a very useful laboratory method for the preparation of various polyamides of the AB or AA-BB type via polycondensation of amino acids and of aromatic or aliphatic dicarboxylic acids with aromatic diamines<sup>5-7)</sup>. The direct polycondensation of imidodicarboxylic acids with diamines using the reaction with triphenyl phosphite has not been reported so far. In the present article, imide-containing dicarboxylic acids (**1**) were first prepared from trimellitic anhydride and amino acids such as glycine,  $\gamma$ -aminobutyric acid, and  $\epsilon$ -aminocaproic acid (Eq. (1)), and then directly polycondensated with various aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents,

producing various aliphatic-aromatic poly(amide-imide)s (Eq. (2)). A facile and more effective synthetic route compared to that reported in the earlier literature<sup>2)</sup> will be described. We also report the factors affecting this reaction system, particularly with regard to the effect on the polycondensation of *N*-(trimellitoyl)glycine (**1-1**) and 4,4'-oxydianiline (**2a**), in view of the type and concentration of metal salts, reactant concentration, and the type of solvent. Moreover, the solubility, thermal properties, and tensile properties of the obtained poly(amide-imide)s will also be depicted.



## Experimental part

### Materials

Trimellitic anhydride (from Wako) was used without previous purification. Amino acids (from TCI) were also used as received.

Commercially obtained anhydrous LiCl and CaCl<sub>2</sub> were dried under vacuum at 150 °C for 6 h and 180 °C for 10 h, respectively. *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 (**2g**) (from Wako) was vacuum distilled before use. The other aromatic diamines were of high purity when received from the manufacturers and used without any further purification. They included 4,4'-oxydianiline (**2a**), 1,4-phenylenedioxydianiline (**2b**), 4,4'-methylenediamine (**2d**), 4,4'-thiodianiline (**2e**), benzidine (**2f**), 4,4'-sulfonyldianiline (**2i**) (the above diamines were supplied by TCI Co.), 3,4'-oxydianiline (**2c**) (from Teijin Ltd., Tokyo), and 3,3'-benzophenonediamine (**2h**) (from Mitsui Toatsu Chemicals Inc.).

Imide-dicarboxylic acids **1** were synthesized by condensation of trimellitic anhydride with amino acids,  $\text{NH}_2-(\text{CH}_2)_m\text{COOH}$ , containing different numbers of methylene groups,  $m = 1, 3, 5$ . As an example, we describe the preparation of 1-1, corresponding to  $m = 1$  for glycine:

19,2 g (0,1 mol) of trimellitic anhydride and 7,5 g (0,1 mol) of glycine 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 for about additional 3 h until about 1,8 ml of water was distilled off azeotropically. On cooling, a white crystalline product separated from the final reaction solution, which was recrystallized from DMF/water. 21 g (84% yield) of pure *N*-(trimellitoyl)glycine (1-1) of m. p. 268 °C were obtained.

IR (KBr): 2500–3000  $\text{cm}^{-1}$  (carboxylic —OH), 1705  $\text{cm}^{-1}$  (carboxylic C=O), 1770 and 1730  $\text{cm}^{-1}$  (imide C=O), 735  $\text{cm}^{-1}$  (imide ring).

$\text{C}_{11}\text{H}_7\text{NO}_6$ (249,2)	Calc.	C 53,02	H 2,83	N 5,62
	Found	C 53,02	H 2,59	N 5,57

The other two imide-diacids were obtained by the same method. 1-3; m. p. 210 °C, yield: 80%. 1-5; m. p. 204 °C, yield: 74%. The elemental analyses of both compounds agree well with the calculated values.

### Polymerization

As a typical experiment of this study, a mixture of 2,49 g (0,01 mol) of *N*-(trimellitoyl)glycine (1-1), 2,00 g (0,01 mol) of 4,4'-oxydianiline (**2a**), 1 g of lithium chloride, 6,21 g (0,02 mol) of triphenyl phosphite, 10 ml of pyridine, and 40 ml of NMP was heated with stirring at 100 °C for 3 h under nitrogen. The produced polymer solution was trickled in 500 ml of methanol, giving rise to a fibrous yellow precipitate, which was washed thoroughly with methanol and water, collected by filtration and dried. Yield of **3a-1**: 3,73 g (99%).  $\eta_{\text{inh}} = 2,65$  dl/g (DMAc/5 wt.-% LiCl,  $c = 0,5$  g/dl, 30 °C).

IR (film): 3300, 1650, and 1560  $\text{cm}^{-1}$  (amide), 1780 and 1720  $\text{cm}^{-1}$  (imide ring, symmetrical and asymmetrical C=O stretching), 720  $\text{cm}^{-1}$  (imide ring deformation).

$(\text{C}_{23}\text{H}_{15}\text{N}_3\text{O}_5)_n$ (413,4) <sub>n</sub>	Calc.	C 66,82	H 3,65	N 10,17
	Found	C 66,78	H 3,43	N 10,04

All other poly(amide-imide)s were prepared in a similar manner.

### Characterization

Melting points of imide-diacids were measured in capillaries on a Yamato m. p. apparatus (Model MP-21) and are uncorrected.

IR spectra were recorded on a Jasco IRA-2 grating infrared spectrophotometer.

Elemental analyses were run in a Perkin-Elmer Model 240 C, H, N analyzer.

Inherent viscosities of all polymers were determined at 0,5 g/dl concentration in DMAc/5 wt.-% LiCl, at 30 °C, using a Cannon-Fenske viscometer.

Qualitative solubility was determined using about 0,2 g of polymer in 2 ml of solvent.

Thermogravimetric data were obtained using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer. Measurements were performed with  $10 \pm 2$  mg samples heated in flowing nitrogen (50  $\text{cm}^3/\text{min}$ ) at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) analyses were performed on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 910 differential scanning calorimeter, in flowing nitrogen ( $30 \text{ cm}^3/\text{min}$ ) at a heating rate of  $10^\circ\text{C}/\text{min}$ .

An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples at a drawing speed of 5 cm/min. Measurements were performed at room temperature (about  $20^\circ\text{C}$ ) with film specimens (5 mm wide, 5 cm long, and about 0,1 mm thick), and an average of at least five individual determination was used.

## Results and discussion

### *Polycondensation*

Yamazaki et al. have described the direct polycondensation reactions of dicarboxylic acids and diamines by using diphenyl<sup>8)</sup> and triaryl phosphites<sup>9)</sup> in the presence of pyridine, producing polyamides with high molecular weight, especially from aliphatic dicarboxylic acids and aromatic diamines. The mechanism has been proposed to include the formation of an *N*-phosphonium salt of pyridine<sup>10)</sup>. Afterwards, they found that the addition of LiCl or CaCl<sub>2</sub> to amide-type solvents led to wholly aromatic polyamides with high molecular weight<sup>5)</sup>. This work presents the results of synthesis of high-molecular-weight poly(amide-imide)s by applying triphenyl phosphite to the polycondensation of aromatic diamines with aliphatic-aromatic imide-containing dicarboxylic acids. The polycondensation reaction of *N*-(trimellitoyl)glycine (**1-1**) and 4,4'-oxydianiline (**2a**) was carried out by using triphenyl phosphite (TPP) in NMP/pyridine solution in the presence of various metal salts (4 wt.-%) at  $100^\circ\text{C}$ . As shown in Fig. 1, the addition of LiCl or CaCl<sub>2</sub> to the reaction medium causes a significant increase of inherent viscosity. The presence of LiBr also causes a favorable effect upon the molecular weight of polymer, though its effect is less than that of LiCl or CaCl<sub>2</sub> at the same amount added. In general, the addition of metal salts like LiCl and CaCl<sub>2</sub> to amide-type solvents, such as NMP, is recognized to prevent precipitation of the polymer produced. Hence, the polymer chain does not cease to grow because of phase separation. For the polycondensation reaction of **1-1** and **2a** in NMP/pyridine solution, a homogeneous reaction state still could be obtained even in the absence of metal salts. However, the inherent viscosity of the final polymer reached 0,7 dl/g only after the reaction was carried out at  $100^\circ\text{C}$  for 3 h. This reflects that metal salts do not only raise the solvating power of solvents but are also involved in the polycondensation reaction, as reported by Yamazaki et al.<sup>5)</sup>. Also from Fig. 1, we can observe that the major increase of viscosity occurs in the first hour of the reaction at  $100^\circ\text{C}$ . Further heating for additional two hours ensures the completion of polycondensation reaction.

Results of the polycondensation of **1-1** and **2a** by using TPP in the presence of various amounts of LiCl or CaCl<sub>2</sub> are shown in Fig. 2, where the concentration of each monomer is 0,2 mol/l in 4:1 by vol. NMP/pyridine solution. A maximum of viscosity was observed at the concentration of around 1 wt.-% for CaCl<sub>2</sub> and 2 wt.-% for LiCl. Further addition caused a decrease of viscosity, in particular in the case of the addition of LiCl. Almost no polymer was obtained in the presence of more than 12 wt.-% LiCl, where the reaction mixtures were deeply colored. The reaction could tolerate higher additive amounts of CaCl<sub>2</sub>, probably due to its less electrophilicity

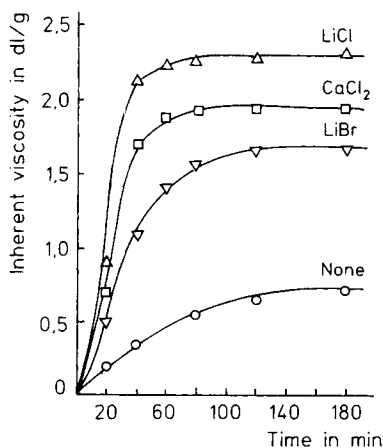


Fig. 1.

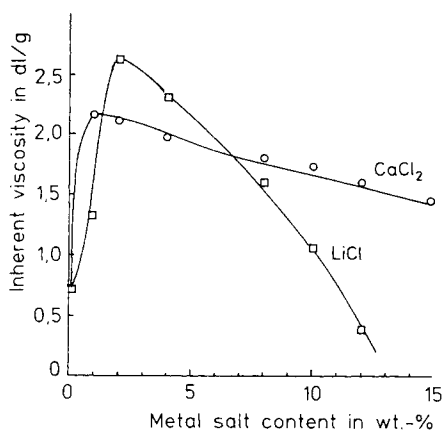


Fig. 2.

Fig. 1. Effect of metal salts (4 wt.-%) on the polycondensation of 1-1 and 2a. Amounts of 1-1 and 2a: 0,01 mol; amount of triphenyl phosphite: 0,02 mol; vol. of pyridine: 10 ml; vol. of NMP: 40 ml; temp.: 100 °C

Fig. 2. Effect of the concentration of metal salts on the polycondensation of 1-1 and 2a. Amounts of 1-1 and 2a: 2,5 mmol; amount of triphenyl phosphite: 5 mmol; vol. of pyridine: 2,5 ml; vol. of NMP: 10 ml; temp.: 100 °C; time: 3 h

toward the solvents. An  $\eta_{inh}$  above 1,5 dl/g still could be obtained at a concentration of  $\text{CaCl}_2$  up to 15 wt.-%.

The effect of varying monomer concentration on the polycondensation reaction of 1-1 and 2a is illustrated in Tab. 1. A maximum of viscosity was observed at a concentration ranging from 0,2–0,3 mol/l of each monomer. At 0,2 mol/l a clear,

Tab. 1. Effect of monomer concentration on the polycondensation of 1-1 and 2a in the presence of 2 wt.-% LiCl<sup>a)</sup>

Monomer conc.		Appearance of reaction mixture	Polymer	
in mol/l	in wt.-%		yield in %	$\eta_{inh}$ <sup>b)</sup> dl/g
0,5	22,4	Gel and precipitate	100	0,92
0,4	17,9	Highly swollen gel	100	2,34
0,3	13,4	Highly viscous	100	2,66
0,2	8,9	Clear, viscous	100	2,65
0,1	4,5	Clear, viscous	99	1,37
0,05	2,2	Clear, non-viscous	95	0,50

a) Amounts of 1-1 and 2a: 5 mmol; amount of TPP: 10 mmol; vol. ratio NMP/pyridine: 4/1; temp.: 100 °C; time: 3 h.

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

viscous polymer solution was obtained. Higher concentration led to a highly viscous state and to a heavy thick gel above 0,4 mol/l. The decrease of inherent viscosity of the resulting polymer at higher monomer concentration may be explained by the reduced reactant mobility due to the onset of gelation or precipitation before high molecular weight could be reached. A lower concentration of the monomer resulted in a less yield of poly(amide-imide) with a lower inherent viscosity. This may be attributed to some competitive side reactions, as discussed by Yamazaki et al.<sup>9)</sup>

The polycondensation reaction of **1-1** and **2a** was investigated in various solvent systems in the presence of 2 wt.-% LiCl (Tab. 2). Among the solvents tested, NMP was most effective, and DMAc gave moderate results, whereas DMF and dimethyl sulfoxide (DMSO) largely retarded the reaction, probably due to the decomposition of DMF and DMSO by LiCl at high temperatures, as indicated by the coloration of the reaction mixture. This indicates that the reaction is affected by the thermal stability of the solvent in the presence of metal salts, like LiCl, at high temperatures.

The viscosity of the resulting poly(amide-imide) varied with the amount of pyridine in NMP, showing the highest value at around 20 vol.-% of pyridine in NMP. Increasing the amount of pyridine caused gelation of the reaction mixture due to the decrease of the solvating power of the solvent system and led to lower viscosity of the final polymer. No high-molecular-weight polymer was obtained when the reaction was carried out in NMP exclusively. This can be readily rationalized by taking into account the lack of *N*-phosphonium salts of pyridine<sup>10)</sup>, which activate the formation of amide linkages.

Several aliphatic-aromatic poly(amide-imide)s from imido-dicarboxylic acids were prepared by carrying out the reaction under the most favorable conditions for the reaction of **1-1** and **2a** (Tab. 3). Almost all polymers were obtained in quantitative yield.

Tab. 2. Polycondensation of **1-1** and **2a** using TPP in various solvent systems containing 2 wt.-% LiCl<sup>a)</sup>

Solvent system		Appearance of reaction mixture	Polymer	
	vol. ratio in ml/ml		yield in %	$\eta_{inh}$ <sup>b)</sup> dl/g
DMSO/Py	(8/2)	Deeply colored	50	0,10
DMF/Py	(8/2)	Colored	92	0,35
DMAc/Py	(8/2)	Clear, viscous	98	1,09
NMP	(10)	Clear, non-viscous	97	0,71
NMP/Py	(8/2)	Clear, viscous	99	2,60
NMP/Py	(6/4)	Clear, viscous	99	2,14
NMP/Py	(4/6)	Slight gelation	99	1,65
NMP/Py	(2/8)	Slight gelation	99	1,68
Py	(10)	Gelation	99	1,58

a) Monomer conc.: 0,2 mol/l, i. e. amounts of **1-1** and **2a**: 2 mmol, vol. of solvent: 10 ml; amount of TPP: 4 mmol; wt. of LiCl: 0,2 g; temp.: 100 °C; time: 3 h.

b) Determined in DMAc/5 wt.-% LiCl at 30 °C at a conc. of 0,5 g/dl.

Tab. 3. Inherent viscosities and elemental analyses of various aliphatic-aromatic poly(amide-imide)s<sup>a)</sup>

Polymer code	Imide-diacid	Diamine	$\eta_{inh}^{b)}$ dl/g	Elemental analyses			
				%C	%H	%N	
3a-1	1-1	2a	2,65	Calc.	66,83	3,65	10,16
				Found	66,78	3,43	10,04
3b-1	1-1	2b	2,14	Calc.	68,66	3,78	8,30
				Found	68,36	3,84	8,02
3c-1	1-1	2c	1,57	Calc.	66,83	3,65	10,16
				Found	66,38	3,67	9,96
3d-1	1-1	2d	1,37	Calc.	70,07	4,16	10,21
				Found	69,87	4,32	10,10
3e-1	1-1	2e	1,67	Calc.	64,33	3,52	9,78
				Found	64,22	4,51	9,59
3f-1	1-1	2f	2,91	Calc.	69,52	3,80	10,57
				Found	69,67	4,15	10,08
3g-1	1-1	2g	1,78	Calc.	63,55	3,45	13,08
				Found	63,83	3,91	12,50
3h-1	1-1	2h	1,82	Calc.	67,76	3,55	9,87
				Found	66,47	3,84	9,72
3i-1	1-1	2i	0,56	Calc.	59,87	3,27	9,10
				Found	59,95	3,53	8,84
3a-3	1-3	2a	1,41	Calc.	68,02	4,34	9,52
				Found	68,67	4,55	9,47
3b-3	1-3	2b	1,77	Calc.	69,78	4,34	7,87
				Found	69,41	4,55	7,86
3c-3	1-3	2c	1,32	Calc.	68,02	4,34	9,52
				Found	67,86	4,30	9,17
3d-3	1-3	2d	1,54	Calc.	71,06	4,81	9,56
				Found	71,06	4,83	9,33
3e-3	1-3	2e	1,20	Calc.	65,63	4,18	9,18
				Found	64,64	4,48	8,91
3f-3	1-3	2f	1,80	Calc.	70,58	4,50	9,87
				Found	69,58	4,65	9,50
3g-3	1-3	2g	1,40	Calc.	65,32	4,33	12,03
				Found	65,60	4,73	12,07
3h-3	1-3	2h	1,71	Calc.	68,87	4,22	9,27
				Found	68,33	4,22	9,02
3i-3	1-3	2i	0,52	Calc.	61,34	3,91	8,58
				Found	61,40	4,08	8,27
3a-5	1-5	2a	1,80	Calc.	69,07	4,94	8,95
				Found	68,97	5,15	8,92
3b-5	1-5	2b	1,75	Calc.	70,58	4,84	7,48
				Found	70,57	4,93	7,45
3c-5	1-5	2c	1,16	Calc.	69,07	4,94	8,95
				Found	68,60	5,05	8,88
3d-5	1-5	2d	1,00	Calc.	71,93	5,39	8,99
				Found	70,93	5,44	8,71
3e-5	1-5	2e	1,10	Calc.	66,79	4,77	8,65
				Found	66,18	4,91	8,33
3f-5	1-5	2f	2,13	Calc.	71,51	5,11	9,26
				Found	70,83	5,15	9,07
3g-5	1-5	2g	1,64	Calc.	66,83	5,07	11,13
				Found	66,40	4,93	10,96
3h-5	1-5	2h	1,25	Calc.	69,84	4,81	8,72
				Found	70,43	5,24	8,42
3i-5	1-5	2i	0,54	Calc.	62,66	4,48	8,12
				Found	62,34	4,60	7,92

a) Polymerization was carried out with 5 mmol of each monomer, 10 mmol of TPP, 5 ml of pyridine, and 0,5 g of LiCl in 20 ml of NMP at 100 °C for 3 h under nitrogen.

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

Most diamines gave poly(amide-imide)s with high viscosity in the reaction with imide-dicarboxylic acids. Exceptionally, 4,4'-sulfonyldianiline (**2i**) yielded low-molecular-weight polymers, probably because of the lower basicity of the amine. The inherent viscosities of the resultant polymers were directed by the reactivity of the diamine and also by the chemical structure of the polymer. The 3-3 and 3-5 series of poly(amide-imide)s with longer flexible methylene groups show lower viscosities than the 3-1 series. For the same series of poly(amide-imide)s, the polymer derived from benzidine (**2f**) shows the highest viscosity, which may be due to the rod-like nature of biphenyl groups. Those polymers derived from oxygen-bridged diamines, such as 4,4'-oxydianiline (**2a**) and 1,4-phenylenedioxydianiline (**2b**), also show high inherent viscosities, probably due to their high reactivity. The lower viscosity of the polymer derived from 3,4'-oxydianiline (**2c**), compared to that derived from **2a**, may be attributed to its semiflexible structure. In interpreting the viscosity behavior, one must bear in mind that the inherent viscosity of a semiflexible polymer is much lower than that of a rigid polymer of the same molecular weight. Results of elemental analyses of various poly(amide-imide)s are also listed in Tab. 3. The analytical values of all polymers agree well with the calculated ones.

#### *Properties of polymers*

The qualitative solubilities of the poly(amide-imide)s are given in Tab. 4. It is found that the nature of the diamine influences the solubility predominantly over that of the aliphatic imide-diacid. Rigid diamine moieties such as biphenyl and *p*-phenylene lower the solubility. All polymers, except for some derived from benzidine (**2f**) and *p*-phenylenediamine (**2g**) and polymers **3a-5** and **3b-5**, show excellent solubility in polar solvents such as DMAc, DMF, NMP, and DMSO. The lower solubility of **3a-5** and **3b-5** in polar solvents may be accounted for by their higher molecular weight and the presence of the longer aliphatic chain in their polymer backbones. The poly(amide-imide)s with longer aliphatic chains show a tendency of increasing solubility in hexamethylphosphoric triamide (HMPA) and *m*-cresol and decreasing solubility in pyridine and sulfolane. All the polymers are soluble in concentrated sulfuric acid. However, they are insoluble in common organic solvents like nitrobenzene, chloroform, dichloromethane, tetrahydrofuran, and acetone. In general, this class of polymers shows better solubility than wholly aromatic poly(amide-imide)s due to the presence of a more flexible aliphatic chain.

The thermal stability and glass transition temperatures ( $T_g$ ) of polymers were evaluated by thermogravimetric analysis (TGA) and DSC, respectively. Contrary to the effect on solubility, the imide-diacid character affects  $T_g$  of polymers predominantly over the diamine character. From the data shown in Tab. 5, the poly(amide-imide)s with longer aliphatic chain exhibit lower  $T_g$ 's, as it could be expected. It is well documented that polymer backbone rigidity can be increased by substituting flexible bridging groups such as —O—, —CH<sub>2</sub>—, etc., by a chain-stiffening group such as a phenyl group. For the polymers derived from the same imide-diacid, those with the diamine moiety of stiff *p*-phenylene linkage show the highest  $T_g$ , while the double oxygen bridging linkage of **2b** moiety causes increased chain flexibility, leading to the lowest



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

Polymer	Solvents <sup>b)</sup>								
	DMAc	DMF	NMP	DMSO	HMPA	Py	<i>m</i> -cresol	sulfolane	H <sub>2</sub> SO <sub>4</sub>
<b>3a-1</b>	+	+	+	+	+h	+	s	sh	+
<b>3b-1</b>	+	+	+	+	-	s	s	-	+
<b>3c-1</b>	+	+	+	+	+h	+	+	+h	+
<b>3d-1</b>	+	+	+	+	+h	+	+	+h	+
<b>3e-1</b>	+	+	+	+	sh	+	s	+h	+
<b>3f-1</b>	+	-	+	s	-	-	-	-	+
<b>3g-1</b>	+	+	+	+	+h	-	-	-	+
<b>3h-1</b>	+	+	+	+	+h	+	+	+h	+
<b>3i-1</b>	+	+	+	+	+h	+	+h	+h	+
<b>3a-3</b>	+	+	+	+	+h	s	+	sh	+
<b>3b-3</b>	+	+	+	+	+	+	+	-	+
<b>3c-3</b>	+	+	+	+	+	+	+	+	+
<b>3d-3</b>	+	+	+	+	+	+	+	+h	+
<b>3e-3</b>	+	+	+	+	-	+	+	-	+
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<b>3g-3</b>	-	-	+	+	+h	-	-	-	+
<b>3h-3</b>	+	+	+	+	+	+	+	+h	+
<b>3i-3</b>	+	+	+	+	+	+	+	+h	+
<b>3a-5</b>	+h	-	+	+h	+	s	+	-	+
<b>3b-5</b>	-	-	-	-	sh	-	-	-	+
<b>3c-5</b>	+	+	+	+	+	+	+	+h	+
<b>3d-5</b>	+	sh	+	+	+	-	+	-	+
<b>3e-5</b>	+	+	+	+	+	-	+	-	+
<b>3f-5</b>	-	-	+h	+h	+	-	-	-	+
<b>3g-5</b>	-	-	+	-	+h	-	-	-	+
<b>3h-5</b>	+	+	+	+	+	+	+	s	+
<b>3i-5</b>	+	+	+	+	+	+	+	+h	+

a) Solubility: +, soluble at room temp.; s, swelling at room temp.; +h, soluble on heating; sh, swelling on heating; -, insoluble. All the polymers are insoluble in nitrobenzene, chloroform, dichloromethane, tetrahydrofuran, and acetone.

b) DMAc (*N,N*-dimethylacetamide); DMF (*N,N*-dimethylformamide); NMP (*N*-methyl-2-pyrrolidone); DMSO (dimethyl sulfoxide); HMPA (hexamethylphosphoric triamide); Py (pyridine).

$T_g$ . Well-defined melting points of most of the polymers could not be obtained by DSC, probably due to their amorphous nature. Anyway, the poly(amide-imide)s with longer aliphatic chain, such as **3a-5** and **3b-5**, show clearer melting points ( $T_m$ ) by DSC (Fig. 3).

Fig. 4 presents typical TG curves of poly(amide-imide)s in nitrogen. From the comparison between polymers **3a-1**, **3a-3**, and **3a-5**, it is found that the number of aliphatic carbons did not cause a significant difference in their initial decomposition temperatures, contrary to what happened in the case of  $T_g$ . There are no great differences in the thermal stability of these aliphatic-aromatic poly(amide-imide)s up

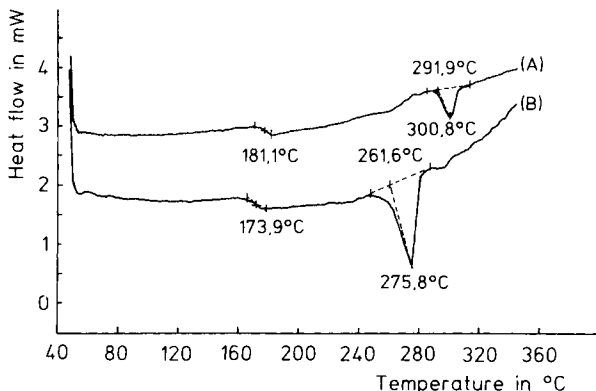


Fig. 3. DSC curves of poly(amide-imide)s **3a-5** (A) and **3b-5** (B), at a heating rate of 10 °C/min in nitrogen

to about 450 °C, beyond which the polymer with a bridging group of one methylene is more stable than that with three or five methylenes. When compared with the wholly aromatic poly(amide-imide) analogue **4**, the aliphatic-aromatic poly(amide-imide)s decompose at lower temperature (by 50–60 °C), whereas the leaving char yield at 800 °C is higher than in the case of **4**. A possible explanation for the latter observation is that in the aliphatic-aromatic poly(amide-imide)s cyclization and crosslinking reactions take place during the heating process, leading to a higher char yield and even a slower decomposition rate, as shown in Fig. 4. The TGA data, temperatures at various percents of weight loss and char yield at 800 °C, of all polymers are summarized in Tab. 5. In general, these polymers show rapid weight loss in the region 400–500 °C in nitrogen. The decomposition temperatures at which 10% weight loss was observed for these poly(amide-imide)s ranged from 422 to 460 °C. Tab. 5 also demonstrates that these polymers undergo extensive carbonization upon non-oxidative degradation, leaving 42.8–63.2% char at 800 °C.

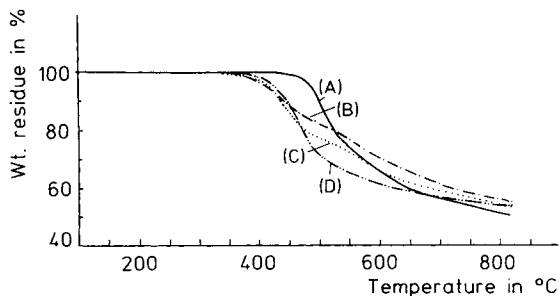
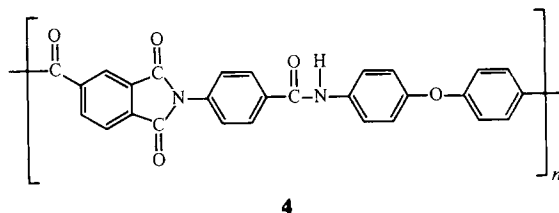


Fig. 4. TG curves of poly(amide-imide)s **3a-1** (B), **3a-3** (C), **3a-5** (D), and **4** (A), at a heating rate of 10 °C/min in nitrogen



Tab. 5. Thermal behavior data of poly(amide-imide)s

Polymer	$T_g$ <sup>a)</sup> °C	Temp. (in °C) with following wt. loss <sup>b)</sup>				Residual wt.-% at 800 °C
		5%	10%	20%	30%	
<b>3a-1</b>	261	411	441	518	600	56,0
<b>3b-1</b>	249	388	422	521	585	56,1
<b>3c-1</b>	256	423	442	503	575	54,6
<b>3d-1</b>	261	410	457	528	605	58,1
<b>3e-1</b>	271	418	454	524	597	56,4
<b>3f-1</b>	268	434	460	510	607	53,7
<b>3g-1</b>	313	430	450	489	554	50,2
<b>3h-1</b>	262	433	456	535	606	56,5
<b>3i-1</b>	306	428	451	510	595	54,8
<b>3a-3</b>	212	418	438	475	567	54,0
<b>3b-3</b>	194	425	447	485	560	51,5
<b>3c-3</b>	197	425	443	469	551	53,2
<b>3d-3</b>	213	420	439	465	528	51,1
<b>3e-3</b>	207	417	435	455	494	49,4
<b>3f-3</b>	216	421	441	530	633	63,2
<b>3g-3</b>	222	405	425	458	545	53,5
<b>3h-3</b>	203	420	446	518	622	61,2
<b>3i-3</b>	215	423	445	469	504	47,8
<b>3a-5<sup>c)</sup></b>	177	429	449	472	509	53,9
<b>3b-5<sup>d)</sup></b>	172	440	457	475	493	46,2
<b>3c-5</b>	172	434	450	470	484	42,8
<b>3d-5</b>	180	432	452	475	495	49,2
<b>3e-5</b>	180	431	448	463	470	38,9
<b>3f-5</b>	181	430	445	472	489	52,0
<b>3g-5</b>	185	413	434	460	473	45,4
<b>3h-5</b>	176	430	452	470	577	51,0
<b>3i-5</b>	179	434	451	472	490	46,3
<b>4</b>	–	486	500	523	573	51,0

a) From DSC measurements conducted at a heating rate of 10 °C/min in nitrogen.

b) Thermogravimetric analyses conducted at a heating rate of 10 °C/min in nitrogen.

c) With  $T_m$  at 292 °C.

d) With  $T_m$  at 261 °C.

Typical stress-strain curves of some poly(amide-imide) films which were cast from the DMAc solutions are shown in Fig. 5, and the tensile properties are summarized in Tab. 6. In tension, some polymer films like **3a-1**, **3b-1**, **3c-1**, and **3g-1** behave as ductile

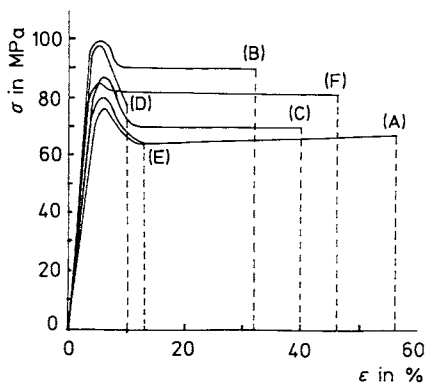


Fig. 5. Stress-strain curves for the 3-1 series of poly(amide-imide)s. (A): 3a-1, (B): 3b-1, (C): 3c-1, (D): 3d-1, (E): 3e-1, (F): 3g-1

materials with a yield point and higher elongation to break. All the tested polymer films show high tensile strengths (above 65 MPa) and high initial modulus (above 1,6 GPa), although some fail in a brittle manner.

Tab. 6. Tensile properties of poly(amide-imide) films

Polymer	Yield strength in MPa	Strength to break in MPa	Elongation to break in %	Initial modulus in GPa
3a-1	80	68	56	1,94
3b-1	99	90	32	2,67
3c-1	87	70	40	2,10
3d-1	89	77	10	2,49
3e-1	77	65	13	1,80
3g-1	85	82	46	2,46
3a-3	81	66	40	1,97
3b-3	89	70	10	1,70
3c-3	—	74	5	1,60
3d-3	89	82	27	2,35
3e-3	—	90	5	2,40
3g-3	84	72	16	2,07
3c-5	98	74	17	2,50
3e-5	—	88	5	2,21

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