

Preparation of poly(amide-imide)s by direct polycondensation with triphenyl phosphite, 3^{a)}

Poly(amide-imide)s based on bis(trimellitimide)s

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SUMMARY:

Six dicarboxylic acids (1a–f) were prepared from trimellitic anhydride and 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-sulfonyldianiline, benzidine, 1,6-hexamethylenediamine, and 4,4'-methylenedicyclohexylamine. These diacids were condensed directly with various aromatic diamines using triphenyl phosphite in 1-methyl-2-pyrrolidone/pyridine solution in the presence of calcium chloride. The inherent viscosity of the polymers is affected by the nature of the diamine and the solubility of the resulting polymers in the reaction media. The highest η_{inh} -value of a poly(amide-imide) obtained was 1.41 dl/g (in *N,N*-dimethylacetamide/5% LiCl at 30 °C). Among the polymers, the wholly aromatic ones show better solubility, higher glass transition temperatures, and higher thermostability than the aliphatic-aromatic ones. Well-defined melting points (T_m) of most wholly aromatic poly(amide-imide)s were not obtained by differential scanning calorimetry (DSC); however, some poly(amide-imide)s containing aliphatic chains showed clear T_m in the first DSC heating traces. Measurements of wide-angle X-ray diffraction revealed that those polymers containing biphenyl or linear hexamethylene groups are partially crystalline. Flexible films with excellent tensile properties were cast from *N,N*-dimethylacetamide solutions of most of the wholly aromatic poly(amide-imide)s.

Introduction

In 1974 Yamazaki et al.^{1,2)} reported on a convenient laboratory method for the preparation of aromatic polyamides which involved complexing of the dicarboxylic acid with tri- or diphenylphosphite and pyridine in a solvent consisting of 1-methyl-2-pyrrolidone (NMP) containing LiCl. The direct synthesis of aliphatic-aromatic poly(amide-imide)s based on *N*-(ω -carboxyalkyl)trimellitimides and wholly aromatic poly(amide-imide)s based on *N*-(carboxyphenyl)trimellitimides by using the Yamazaki phosphorylation procedure, has been described in the previous parts of this series^{3,4)}. These poly(amide-imide)s were prepared by the direct polycondensation of imide-containing dicarboxylic acids and aromatic diamines using triphenyl phosphite and pyridine as condensing reagents in NMP in the presence of metal salts. This synthetic approach of using diacids containing preformed imide rings as monomers offers some advantages over the conventional two-step procedures, via polyamic-acid, and the imide-containing diacyl chloride routes^{5,6)}. The most remarkable one is the achievement of poly(amide-imide)s in solution without needing a thermal curing to

^{a)} Part 2: cf. 3).

assure the closing of imide rings and, meanwhile, without troublesome problems of preparing the acid chlorides. Through the phosphorylation reaction routes, high-molecular-weight aliphatic-aromatic poly(amide-imide)s with η_{inh} up to 2,91 dl/g (in DMAc/5% LiCl at 30 °C) and wholly aromatic ones with η_{inh} up to 1,7 dl/g have been prepared in our previous works of this series^{3,4}.

The present work had the purpose of extending the previous studies to poly-(amide-imide)s derived from bis(trimellitimide)s **1a–f** and various aromatic diamines.

Experimental part

Materials: Trimellitic anhydride was used without previous purification. *p*-Phenylenediamine was vacuum-distilled before use. All other diamines were of high purity when received from the manufacturers and used without any further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. 1-Methyl-2-pyrrolidone (NMP), *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 was purified by vacuum-distillation.

Bis(trimellitimide)s 1a–f: The bis(trimellitimide)s were synthesized by condensation of an α,ω -diamine with trimellitic anhydride in a 1:2 mole ratio. As an example, we describe the preparation of bis(*N,N*-trimellitoyl)-4,4'-oxydianiline (**1a**):

20,0 g (0,1 mol) of 4,4'-oxydianiline and 38,4 g (0,2 mol) of trimellitic anhydride were heated in 150 ml of dry DMF to 60 °C for 1 h. About 50 ml of toluene was then added, and the mixture was heated with reflux for about 3 h until about 3,6 ml of water was distilled off azeotropically under a Dean-Stark trap. After cooling, the precipitated diimide-diacid **1a** was isolated by filtration and recrystallized from *N,N*-dimethylacetamide (DMAc). After isolation by filtration, the purified product was dried *in vacuo*.

By the identical method the other bis(trimellitimide)s **1b–f** were obtained and characterized. Yields and properties of **1a–f** are summarized in Tab. 1.

Polymerization: A typical example of polymerization was as follows. A mixture of 1,37 g (2,5 mmol) of **1a**, 0,50 g (2,5 mmol) of 4,4'-oxydianiline (**2a**), 2 g of calcium chloride, 1,61 g (5,2 mmol) of triphenyl phosphite, 3,3 ml of pyridine, and 13,3 ml of NMP was heated with stirring at 100 °C for 3 h under nitrogen. The obtained polymer solution was trickled on 500 ml of methanol giving rise to a fibrous, yellow precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative. Inherent viscosity of the polymer (in DMAc with dissolved 5 wt.-% LiCl) was 1,24 dl/g, measured on a concentration of 0,5 g/dl at 30 °C.

Other poly(amide-imide)s were synthesized analogously. The inherent viscosities and elemental analyses of the obtained polymers are shown in Tabs. 2 and 3, respectively.

Measurements: Inherent viscosities of the poly(amide-imide)s were determined at 30 °C using 0,5 g/dl solutions of 5 wt.-% LiCl in DMAc or conc. sulfuric acid. Cannon-Fenske viscosimeter were used without kinetic energy correction, since the solvent flow time exceed 100 s.

IR spectra were recorded on a Jasco IRA-2 Grating Infrared Spectrophotometer.

Elemental analyses were carried out with a Perkin-Elmer 240C microanalyzer.

Thermogravimetry was done on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer. Experiments were performed on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 10 °C/min.

DSC was performed on a DuPont 910 differential scanning calorimeter coupled to a DuPont 1090 thermal analyzer at the rate of 10 °C/min in flowing nitrogen (30 cm²/min).

Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered CuK α radiation (40 kV, 15 mA). The scanning rate was 2°/min. Measurements were performed with powder sample (for polymer **9a**) or on film specimens of about 0,5 mm thickness.

Tab. 1. Yields and properties of the diimide-diacids **1a–f**

Com- pound	Yield in %	M. p. ^{a)} in °C	Formula (mol. weight)	Elemental analysis			
				Calc.	C	H	N
1a	75	378	C ₃₀ H ₁₆ N ₂ O ₉ (548,46)	Calc.	65,69	2,94	5,10
				Found	65,52	2,98	5,35
1b	80	360	C ₃₁ H ₁₈ N ₂ O ₈ (546,47)	Calc.	68,13	3,32	5,12
				Found	68,14	3,27	5,22
1c	83	364	C ₃₀ H ₁₆ N ₂ O ₁₀ S (596,53)	Calc.	60,40	2,70	4,69
				Found	60,02	2,92	4,64
1d	85	402	C ₃₀ H ₁₆ N ₂ O ₈ (532,46)	Calc.	67,67	3,02	5,26
				Found	67,66	2,98	5,35
1e	72	306	C ₂₄ H ₂₀ N ₂ O ₈ (464,42)	Calc.	62,07	4,34	6,03
				Found	61,95	4,03	5,96
1f	68	306	C ₃₁ H ₂₆ N ₂ O ₈ (554,54)	Calc.	67,14	4,72	5,05
				Found	67,06	4,58	5,09

a) Determined by DSC with a heating rate of 10 °C/min under nitrogen.

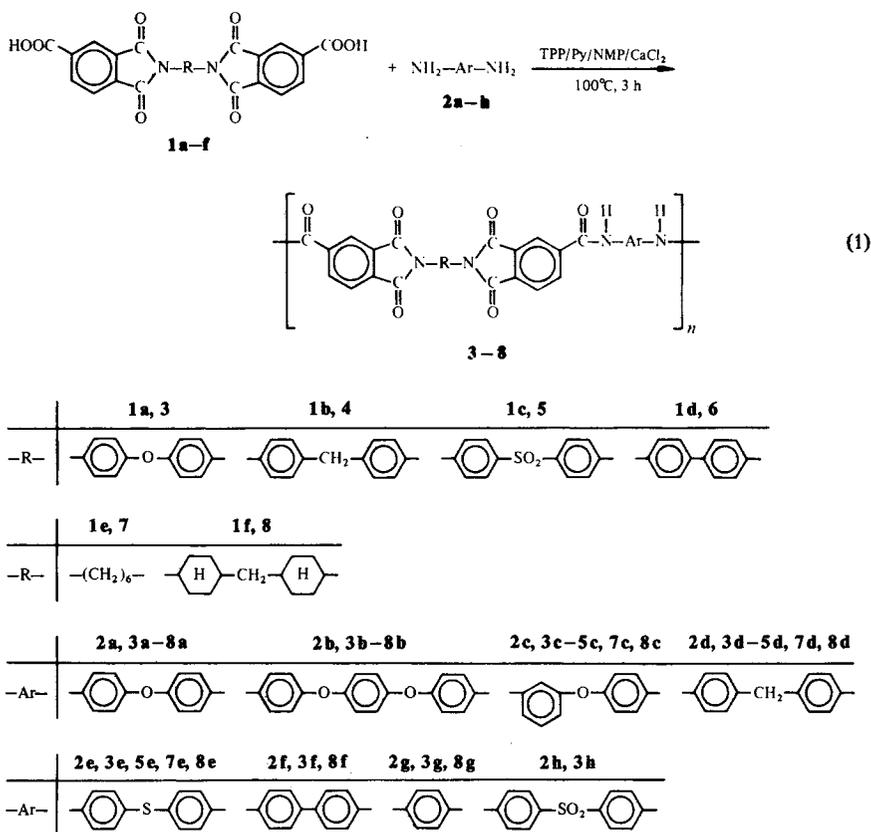
An Instron Universal Tester Model 1130 with a load cell 5 Kg was used to study the stress-strain behavior of the samples at a drawing rate of 5 cm/min. Measurements were performed at room temperature (about 20 °C) with film specimens (0,5 cm wide, 5 cm long, and about 0,1 mm thick) and an average of at least five individual determination was used.

Results and discussion

Syntheses

The bis(trimellitimide)s **1a–f** were synthesized from the corresponding diamines and trimellitic anhydride. Complete cyclization of the intermediate amino acids was achieved by toluene-water azeotropic distillation. The diacid **1e** was already described in the literature^{7–9}). Furthermore, the diacid chlorides of **1a** and **1c** were used for the preparation of various poly(amide-imide)s by Wrasidlo and Augl³), yet the properties of these two diacids were not described. Therefore, melting points and elemental analyses of all diacids used in this work were determined and summarized in Tab. 1 (Exptl. part).

The recrystallized diacids **1a–f** were condensed directly with various aromatic diamines in the mixture of NMP and pyridine in the presence of triphenyl phosphite (TPP) and calcium chloride at 100 °C (Eq. (1)). All poly(amide-imide)s were isolated as yellowish materials with almost quantitative yields; their inherent viscosities are summarized in Tab. 3. The reaction has been proposed to proceed via an acyloxy *N*-phosphonium salt of pyridine followed by aminolysis²). The inherent viscosity of the final polymer is dependent upon such factors as the nature of monomer, monomer concentration, reaction temperature, solvent composition, and stoichiometry. Numerous experiments in which solvent, additive amount of calcium chloride, monomer con-



TPP: triphenyl phosphite

Py: pyridine

NMP: 1-methyl-2-pyrrolidone

centration, temperature, etc. were varied convinced us that the conditions listed in Tab. 3 have been optimized.

The first series of poly(amide-imide)s **3a-h**, listed in Tab. 3 were prepared in an attempt to investigate the effect of diamine nature on the phosphorylation reaction. High-molecular-weight poly(amide-imide)s with η_{inh} of 0.87–1.24 dl/g, except for polymers **3f** and **3h**, were obtained. The lower inherent viscosity of **3f** may be attributable to its low solubility due to the presence of rigid rod-like benzidine (**2f**) moiety, as indicated by the early precipitation during polymerization. Increasing the amount of NMP, used as solvent in order to carry out the reaction in a homogeneous phase, has met with failure in raising the molecular weight of polymer **3f**. The unsatisfactory result obtained from 4,4'-sulfonyldianiline (**2h**) may be explained by its lower basicity due to the presence of the electron-withdrawing sulfonyl group. The more satisfactory results obtained from diamine **2a** and 1,4-phenylenedioxydianiline (**2b**) may be due to their high reactivity and the excellent solubility of their resulting

Tab. 2. Elemental analyses of poly(amide-imide)s

Polymer	Formula	(Mol. weight)	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
3a	(C ₄₂ H ₂₄ N ₄ O ₈) _n	(712,67) _n	70,78	3,39	7,86	70,34	3,43	7,56
3b	(C ₄₈ H ₂₈ N ₄ O ₉) _n	(804,77) _n	71,64	3,50	6,96	71,50	3,63	6,82
3c	(C ₄₂ H ₂₄ N ₄ O ₈) _n	(712,67) _n	70,78	3,39	7,86	70,40	3,40	7,66
3d	(C ₄₃ H ₂₆ N ₄ O ₇) _n	(710,47) _n	72,69	3,69	7,88	72,03	3,60	7,54
3e	(C ₄₂ H ₂₄ N ₄ O ₇ S) _n	(728,46) _n	69,25	3,32	7,69	68,67	3,57	7,04
3f	(C ₄₂ H ₂₄ N ₄ O ₇) _n	(696,67) _n	72,41	3,47	8,04	71,93	3,58	7,89
3g	(C ₃₆ H ₂₀ N ₄ O ₇) _n	(620,57) _n	69,68	3,24	9,03	69,65	3,22	8,97
3h	(C ₄₂ H ₂₄ N ₄ O ₉ S) _n	(760,74) _n	66,31	3,18	7,36	65,77	3,34	7,02
4a	(C ₄₃ H ₂₆ N ₄ O ₇) _n	(710,68) _n	72,67	3,68	7,88	72,13	3,73	7,57
4b	(C ₄₉ H ₃₀ N ₄ O ₈) _n	(802,78) _n	73,31	3,76	6,98	73,58	3,73	6,87
4c	(C ₄₃ H ₂₄ N ₄ O ₇) _n	(710,68) _n	72,67	3,68	7,36	71,78	4,02	6,97
4d	(C ₄₄ H ₂₈ N ₄ O ₆) _n	(708,48) _n	74,59	3,98	7,91	74,08	4,10	7,07
5a	(C ₄₂ H ₂₄ N ₄ O ₉ S) _n	(760,94) _n	66,31	3,18	7,36	65,30	3,57	6,89
5b	(C ₄₈ H ₂₈ N ₄ O ₁₀ S) _n	(852,84) _n	67,60	3,31	6,57	67,56	3,39	6,34
5c	(C ₄₈ H ₂₄ N ₄ O ₁₀ S) _n	(760,94) _n	66,31	3,18	7,36	65,48	3,42	6,94
5d	(C ₄₂ H ₂₄ N ₄ O ₈ S ₂) _n	(776,80) _n	64,94	3,11	7,21	63,88	3,87	6,50
5e	(C ₃₆ H ₂₀ N ₄ O ₈ S) _n	(668,64) _n	64,66	3,01	8,38	64,03	3,58	8,02
6a	(C ₄₂ H ₂₄ N ₄ O ₇) _n	(696,67) _n	72,41	3,47	8,04	71,95	3,99	7,67
6b	(C ₄₂ H ₂₄ N ₄ O ₇) _n	(696,67) _n	72,41	3,47	8,04	71,89	4,10	7,50
7a	(C ₃₆ H ₂₈ N ₄ O ₇) _n	(628,63) _n	68,78	4,49	8,91	67,78	5,01	8,66
7b	(C ₄₂ H ₃₂ N ₄ O ₈) _n	(720,73) _n	69,99	4,47	7,77	69,56	4,68	7,67
7c	(C ₃₆ H ₂₈ N ₄ O ₇) _n	(628,63) _n	68,78	4,49	8,91	68,67	4,50	8,88
7d	(C ₃₇ H ₃₀ N ₄ O ₆) _n	(626,43) _n	70,94	4,82	8,94	70,90	4,78	8,83
7e	(C ₃₀ H ₂₄ N ₄ O ₆) _n	(536,53) _n	67,16	4,51	10,44	66,54	4,67	9,78
8a	(C ₄₃ H ₃₄ N ₄ O ₇) _n	(718,75) _n	71,85	4,76	7,79	71,78	4,70	7,75
8b	(C ₄₉ H ₃₈ N ₄ O ₈) _n	(810,85) _n	72,58	4,72	6,91	72,50	4,68	6,77
8c	(C ₄₃ H ₃₄ N ₄ O ₇) _n	(718,75) _n	71,85	4,76	7,79	71,70	4,63	7,50
8d	(C ₄₄ H ₃₆ N ₄ O ₆) _n	(716,55) _n	73,75	5,06	7,81	73,95	5,23	7,79
8e	(C ₄₃ H ₃₄ N ₄ O ₆ S) _n	(734,81) _n	70,28	4,66	7,62	69,53	5,10	7,34
8f	(C ₃₇ H ₃₀ N ₄ O ₆) _n	(626,65) _n	70,91	4,82	8,94	70,02	5,02	8,56

polymers. Furthermore, the lower inherent viscosity value of the polymer derived from 3,4'-oxydianiline (**2c**) compared to that from **2a** does not necessarily imply a lower molecular weight, since this polymer has a more flexible structure.

In the synthesis of other series of polymers, only some typical diamines were used as monomers. During the synthesis of the two series of polymers **4a–d** and **5a–e**, more favorable results were obtained by using a lower monomer concentration of about 0,1 mol/l. Higher concentrations produced gelation and yielded polymers of low molecular weight. It was interesting to note that sulfone-containing poly(amide-imide)s

Tab. 3. Preparation of various poly(amide-imide)s^{a)}

Polymer	Polymer component		Polymerization		$\eta_{inh}^b)$ of polymer in dl/g	
	diimide-diacid	diamine	monomer conc. in mol/l	appearance of reaction mixture		
3a	1a	2a	0,15	(10,2)	Highly viscous	1,24
3b		2b	0,13	(9,7)	Highly viscous	1,17
3c		2c	0,12	(8,4)	Clear, viscous	0,94
3d		2d	0,10	(7,0)	Clear, viscous	0,87
3e		2e	0,15	(10,4)	Clear, viscous	0,92
3f		2f	0,05	(4,1)	Precipitated	0,32 ^{c)}
3g		2g	0,08	(5,3)	Clear, viscous	1,03
3h		2h	0,15	(11,9)	Clear, nonviscous	0,35
4a	1b	2a	0,10	(7,5)	Clear, viscous	0,77
4b		2b	0,10	(8,4)	Clear, viscous	0,78
4c		2c	0,10	(7,5)	Clear, viscous	0,65
4d		2d	0,10	(7,0)	Clear, viscous	0,60
5a	1c	2a	0,10	(7,9)	Clear, viscous	0,83
5b		2b	0,10	(8,8)	Clear, viscous	0,85
5c		2c	0,10	(7,9)	Clear, viscous	0,76
5d		2e	0,10	(8,1)	Clear, viscous	0,67
5e		2g	0,10	(7,0)	Clear, viscous	0,70
6a	1d	2a	0,05	(3,6)	Precipitated	0,26 ^{c)}
6b	1d	2c	0,05	(3,6)	Precipitated	0,20 ^{c)}
7a	1e	2a	0,20	(13,3)	Highly viscous	1,33
7b		2b	0,20	(15,1)	Highly viscous	1,41
7c		2c	0,20	(13,3)	Clear, viscous	1,03
7d		2d	0,20	(13,2)	Clear, viscous	1,13
7e		2g	0,10	(5,7)	Precipitated	0,19 ^{c)}
8a	1f	2a	0,20	(15,1)	Highly viscous	1,04
8b		2b	0,20	(16,9)	Highly viscous	0,95
8c		2c	0,20	(15,1)	Clear, viscous	0,70
8d		2d	0,20	(15,0)	Clear, viscous	0,82
8e		2e	0,20	(15,4)	Clear, viscous	0,68
8f		2g	0,10	(6,6)	Precipitated	0,18 ^{c)}

a) Amounts of diimide-diacid and diamine: 2,5 mmol; amount of TPP: 5,0 mmol; vol. ratio NMP/Py: 4/1; conc. of CaCl₂: 12 wt.-%, corresponding to the solvent; temp.: 100 °C; time: 3 h.

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

c) Measured in conc. sulfuric acid.

5a–e with moderately high inherent viscosity could be prepared from sulfone-containing diimide-diacid 1c and the corresponding diamines. As described above, it was difficult to prepare high-molecular-weight sulfone-containing polymer 3h from diacid 1a and diamine 2h because of the lower basicity of the diamine.

Diacid 1d exhibits the rigid rod-like nature due to the presence of a biphenyl group. Less favorable results were obtained by reacting it with diamine 2a or 2c even with a

low monomer concentration of 0,05 mol/l, probably caused by the early precipitation of reaction media retarding further polymerization. However, it could be improved by reacting the mixtures of **1d** and terephthalic acid (TPA) or isophthalic acid (IPA) with diamines like **2a**. As shown in Tab. 4, more satisfactory results could be produced from the mixed diacids containing more than 70 mol-% TPA or IPA. These can be explained by the increase of solubility of the obtained copolymers by incorporating higher

Tab. 4. Poly(amide-imide)s prepared from diamine **2a** with mixtures of diacid **1d** and terephthalic acid (TPA) or isophthalic acid (IPA)^{a)}

Polymer (sample)	Polymer component		Monomer conc. in mol/l (wt.-%)	$\eta_{inh}/(\text{dl/g})^c$	
	mixed diacids ^{b)} (mole ratio)	diamine		DMAc 5% LiCl	conc. H ₂ SO ₄
9 (a)	1d/TPA (1/1)	2a	0,05 (3,2) ^{d)}	Insol.	0,48
			0,16 (7,6)	1,10	1,10
			0,20 (8,0)	1,20	1,28
10 (a)	1d/IPA (1/1)	2a	0,05 (3,2) ^{d)}	Insol.	0,43
			0,14 (6,8)	0,73	0,82
			0,20 (8,0)	0,85	1,01

a) Amounts of mixed diacids and **4a**: 2,5 mmol; amount of TPP: 5,2 mmol; vol. ratio NMP/Py: 4/1; conc. of CaCl₂: 12 wt.-%, corresponding to the solvent; temp.: 100 °C; time: 3 h.

b) TPA: terephthalic acid; IPA: isophthalic acid.

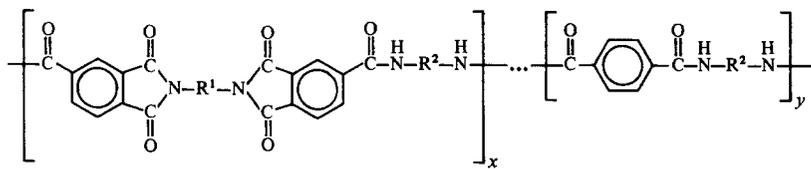
c) Measured at 30 °C on a concentration of 0,5 g/dl.

d) Precipitation occurred during reaction.

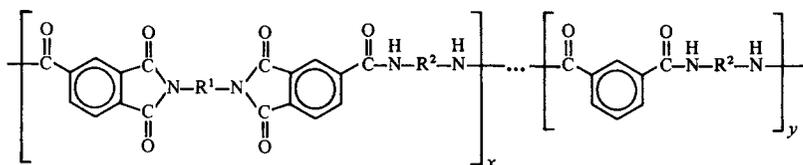
proportions of amide linkages in the polymer backbones. Poly(amide-imide)s containing more than 50% **1d** in the mixed diacids precipitated rapidly from the polymerization medium. Copolymers **9** and **10**, containing 50% of **1d** monomeric units, are insoluble in DMac/5 wt.-% LiCl and have a lower inherent viscosity of 0,48 and 0,43 dl/g, respectively, in conc. sulfuric acid.

Moderate to high-molecular-weight, aromatic-aliphatic poly(amide-imide)s **7a–d** and **8a–e** could be synthesized from the corresponding diimide-diacids and diamines with a higher monomer concentration of 0,2 mol/l. However, polymers **7e** and **8f**, derived from *p*-phenylenediamine (**2g**), were obtained with low molecular weights. This result led us to consider again that higher solubility of polymer favors polycondensation.

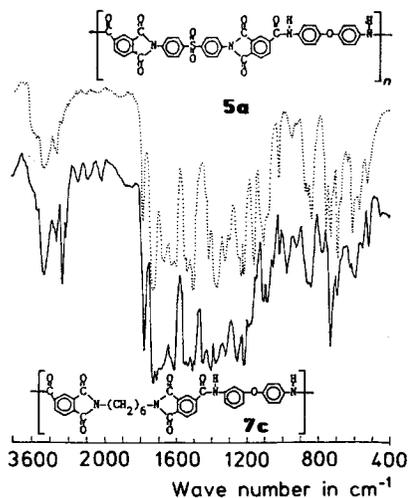
The compositions and structures of these polymers were confirmed by their elemental analyses and IR spectra. As shown in Tab. 2 (Exptl. part), the elemental analyses are in good agreement with the calculated values. Fig. 1 shows the typical IR spectra of polymers **5a** and **7c**. The IR spectra show the characteristic absorption bands for the imide ring at 1780 and 1720 cm⁻¹ due to the asymmetrical and symmetrical C=O stretching vibration, and at 1100 and 720 cm⁻¹, due to ring deformation. Bands of amide groups appear at approximately 3300, 1650, and 1550 cm⁻¹.



9



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Fig. 1. IR spectra of poly(amide-imide)s **5a** and **7c**

Properties of the polymers

The solubilities of some typical poly(amide-imide)s, derived from diamine **2a** and the corresponding diacids, are listed in Tab. 5. The aromatic poly(amide-imide)s **3a**, **4a**, and **5a**, except the highly rigid **6a**, are readily soluble in amide-type solvents, such as DMAc, dimethyl sulfoxide (DMSO), NMP, and 1,3-dimethyl-2-imidazolidone (DMI), and soluble in hexamethylphosphoric triamide (HMPT) on heating. Especially, sulfonyl-containing **5a** shows the best solubility, being soluble in all the solvents tested. The solubility behavior of aromatic-aliphatic poly(amide-imide)s **7a** and **8a** is quite different from that of wholly aromatic ones. Polymer **7a**, with a linear aliphatic hexamethylene chain, reveals very poor solubility in the polar amide-type solvents. It is only soluble in DMAc containing 5 wt.-% LiCl on heating, whereas, cyclohexamethy-

lene-containing **8a** shows a slightly better solubility than **7a**. It is soluble in HMPT and DMAc containing 5 wt.-% LiCl at room temperature and soluble in NMP and DMI on heating. Moreover, all the polymers listed in Tab. 5 are insoluble in common organic solvents, such as acetone, tetrahydrofuran, chloroform, nitrobenzene, etc.; however, they are all soluble in conc. sulfuric acid.

The poly(amide-imide)s were thermally characterized by means of TG and DSC. Fig. 2 shows typical TG curves in nitrogen of some poly(amide-imide)s derived from

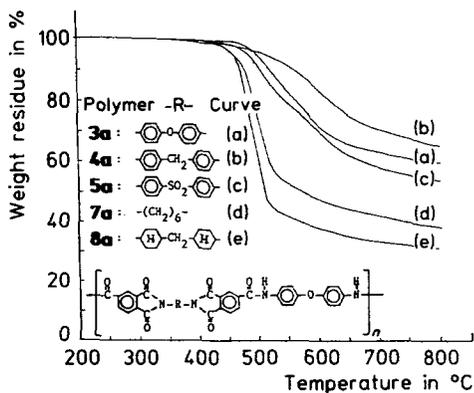
Tab. 5. Solubility of poly(amide-imide)s from diamine **2a**^{a)}

Solvent ^{b)}	Polymer					
	3a	4a	5a	6a	7a	8a
DMAc	+	+	+	-	-	-
DMAc + 5% LiCl	+	+	+	-	+h	+
DMF	s	-	+	-	-	-
DMSO	+	+	+	-	-	-
NMP	+	+	+	-	-	+h
DMI	+	+	+	-	-	+h
HMPT	+h	+h	+h	-	-	+
Pyridine	-	-	+	-	-	-
<i>m</i> -Cresol	-	+h	+h	-	-	sh
Sulfolane	-	sh	+h	-	-	-
Conc. sulfuric acid	+	+	+	+	+	+

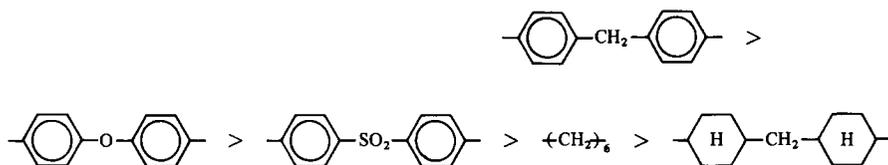
a) +: soluble at room temperature; s: swelling at room temperature; +h: soluble on heating; sh: swelling on heating; -: insoluble.

b) DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfide; NMP: 1-methyl-2-pyrrolidone; DMI: 1,3-dimethyl-2-imidazolidone; HMPT: hexamethylphosphoric triamide.

Fig. 2. TG curves of poly(amide-imide)s from diamine **2a**, with a heating rate of 10 °C/min in nitrogen



diamine **2a** with a heating rate of 10 °C/min under flowing nitrogen. The nature of linking group between two trimellitimide units of the diimide-diacids seems to play a significant role and diminishes the thermal stability in the order:



The presence of an aliphatic chain in polymer backbones of **7a** and **8a** led to a lower initial decomposition temperature and rapid decomposition around 450–500 °C. Wholly aromatic poly(amide-imide)s of **3a**, **4a**, and **5a** evidently show higher thermal stability and undergo extensive carbonization upon nonoxidative degradation leaving more than 50% char at 800 °C. TG data analyzed in nitrogen and in air of some poly(amide-imide)s are summarized in Tab. 6. Almost all polymers decompose earlier in air than in nitrogen by about 20–60 °C (at 5 wt.-% loss). However, it is noted that polymers **7a** and **c** show a very similar TG behavior in both nitrogen and air atmospheres.

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

Polymer	DSC		TG ^{c)}						
	$T_g/^\circ\text{C}^{\text{a)}$	$T_m/^\circ\text{C}^{\text{b)}$	temp. (in °C) at various wt.-loss						residual wt.-% at 800 °C in N ₂
			in N ₂			in air			
5%	10%	30%	5%	10%	30%	5%	10%	30%	
3a	274	444 (s)	500	525	614	467	507	581	59,5
3b	260	no	513	567	661	462	506	555	59,2
3c	236	no	514	573	682	493	560	648	62,8
3d	270	no	454	516	709	401	493	615	66,3
3e	284	no	506	558	667	479	521	573	59,5
3g	no ^{d)}	no	515	535	620	497	534	597	58,2
4a	251	no	507	562	697	475	550	620	64,8
5a	252	no	484	506	603	427	488	571	54,3
5b	243	no	494	526	628	472	514	606	59,0
7a	198	346 (s)	453	479	506	449	475	506	37,8
7c	190	336 (b)	472	485	508	468	483	507	42,6
8a	250	411 (s)	460	472	495	397	419	485	30,2

a) From the second heating traces of DSC measurements conducted with a heating of 10 °C/min in nitrogen.

b) Temperatures of the endotherm peaks in the first heating trace of DSC measurements; s: sharp peak; b: broad peak.

c) Thermogravimetry was conducted at a heating rate of 10 °C/min.

d) Not observed before decomposition.

Tab. 6 also summarizes the thermal transition data of the poly(amide-imide)s. Glass transition temperatures (T_g) were recorded at 274, 251, 252, 198, and 250 °C for polymers **3a**, **4a**, **5a**, **7a**, and **8a**, respectively. As it could be expected, poly(amide-imide) **7a** with a linear aliphatic chain exhibits lower T_g . Well-defined melting points of most wholly aromatic polymers listed in Tab. 6 could not be obtained by DSC, probably due to their amorphous nature. Anyway, the poly(amide-imide)s with an aliphatic chain, such as **7a** and **8a**, show clear melting points (T_m) by DSC. The DSC traces of polymer **7a** show a sharp endotherm peak at 346 °C (Fig. 3). Cooling and reheating show a strong T_g at 198 °C and disappearance of the melting transition. Annealing does not alter the intensity and position of the endotherm peak to any significant extent, implying that this polymer is inherently slow in crystallization. A similar phenomenon was observed for other crystallizable polymers. One apparent reason is the presence of the trimellitimide unit which leads to structure irregularity.

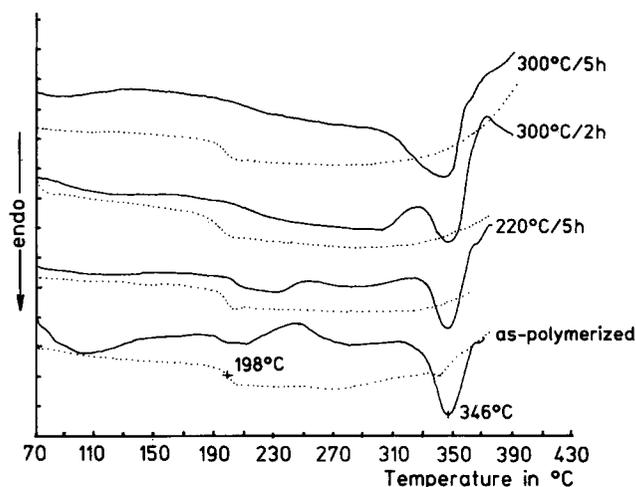


Fig. 3. DSC thermograms of poly(amide-imide) **7a** obtained before and after annealing. (—): First heating, (...): second heating

X-ray diffractograms of some representative polymers (polymer **3a**, **4a**, **5a**, **7a**, **7c**, **8a**, and **9a**) are shown in Fig. 4. Among those poly(amide-imide)s derived from diamine **2a**, the wholly aromatic ones, except polymer **9a**, exhibit amorphous patterns. The crystalline nature of polymer **9a** can be attributed to the relatively rigid orientation of the polymer chains due to the presence of biphenyl and terephthaloyl groups. Among the aliphatic-aromatic poly(amide-imide)s, polymer **7a** shows a crystalline pattern, which may be attributable to better package of polymer chains due to the presence of linear aliphatic chain. Polymer **8a**, containing cycloaliphatic chains, shows less crystalline behavior than **7a**, and polymer **7c**, containing a linkage in *meta*-position, has an amorphous nature. The poly(amide-imide)s showing crystalline

patterns are insoluble in common organic solvents, which is in contrast to the general rule that the solubility decreases with increasing crystallinity.

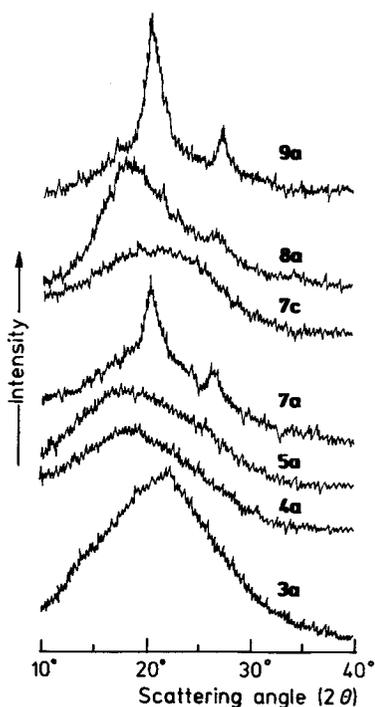


Fig. 4. Wide-angle X-ray diffractograms of some poly(amide-imide)s

Strong and flexible films could be cast from the DMAc solutions of most of the obtained wholly aromatic poly(amide-imide)s, except for those polymers containing a biphenyl group. The tensile properties of some typical poly(amide-imide)s are summarized in Tab. 7. In tension, some polymer films like **3a**, **c** and **4a** behave as a

Tab. 7. Tensile properties of poly(amide-imide) films

Polymer ^{a)}	Strength at yield in MPa	Strength at break in MPa	Elongation to break in %	Initial modulus in GPa
3a	88	84	20	1,96
3c	111	92	13	2,53
4a	84	78	15	1,81
5a	—	92	9	1,80
5b	—	88	5	2,21
7c	78	55	31	1,80
8a ^{b)}	—	101	7	2,02

a) Films were cast from polymer solutions of DMAc.

b) Cast from polymer solution of DMAc containing dissolved 1 wt.-% LiCl.

ductile material with a yield point and moderate elongation to break, while sulfonyl-containing polymers **5a** and **b** fail in a brittle manner, probably due to the stronger interaction between their polymer chains caused by SO₂ groups. Because of the poor solubility of the aliphatic-aromatic poly(amide-imide)s, it is difficult to process them by solution-casting. However, those polymers with unsymmetrical structure might be solution-processable. Typical mechanical properties of a cast film of **7c** are a tensile strength on yield of 78 MPa, a strength at break of 55 MPa, an elongation at break of 31%, and a tensile modulus of 1,8 GPa. The longer elongation of **7c** may be attributed to the presence of linear aliphatic groups in its polymer chain.

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