

New poly(amide-imide) syntheses, 3^{a)}

Preparation and properties of cardo poly(amide-imide)s derived from 9,9-bis(4-aminophenyl)fluorene, trimellitic anhydride, and various aromatic diamines

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SUMMARY:

An imide-ring-containing dicarboxylic acid, *N,N'*-(9-fluorenylidenedi-1,4-phenylene)diphthalimide-4-carboxylic acid (**1**), was prepared by condensation of trimellitic anhydride and 9,9-bis(4-aminophenyl)fluorene. A series of new aromatic cardo poly(amide-imide)s having inherent viscosities of 0,59–1,13 dL/g were prepared by the direct polycondensation of this diimide-diacid with various aromatic diamines using triphenyl phosphite and pyridine as condensing agents in 1-methyl-2-pyrrolidone (NMP) in the presence of calcium chloride. The polymers are amorphous and readily soluble in highly polar solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, NMP, and *m*-cresol. Transparent and tough films can be easily cast from the polymer solutions. The glass transition temperatures of these poly(amide-imide)s are above 320 °C. Thermal analyses indicated that these polymers are fairly stable, and the 10% weight loss temperatures were recorded in the range of 532–622 °C in nitrogen atmosphere.

Introduction

Although aromatic polyimides are well recognized as a class of thermally stable engineering materials, their widespread use is limited due to poor handling and processing characteristics. To overcome these difficulties, various copolyimides have been developed. For example, poly(amide-imide)s were developed as alternative materials that offer a compromise between excellent thermal stability and processability.

Different methods have been reported for the synthesis of poly(amide-imide)s^{1–8)}. Recently, we have successfully applied the Yamazaki phosphorylation polyamidation reaction⁹⁾ to the synthesis of poly(amide-imide)s, by the direct polycondensation of dicarboxylic acids having a preformed imide ring, with aromatic diamines using triphenyl phosphite and pyridine as condensing agents^{10–13)}. Very recently, we have applied this method to the screening of new poly(amide-imide)s^{14, 15)} due to its particular advantages. Continuing these studies, this paper deals with the synthesis of a series of novel poly(amide-imide)s from trimellitic anhydride, 9,9-bis(4-aminophenyl)fluorene, and other aromatic diamines.

Polymers containing a repeating unit that includes a cyclic side group, for example, a phthalide, a phthalimidine, or a fluorene group, have been proposed to be termed

^{a)} Part 2: cf. ¹⁵⁾

cardo polymers from the Latin "cardo" (a loop), since such groups can be considered as loops at the backbone of the macromolecule. Korshak et al.¹⁶⁾ demonstrated that the introduction of cardo groups into the polymer chain of aromatic polyesters, polyethers, polyamides, and heterocyclic polymers endowed them with enhanced thermal stability together with excellent solubility, which is of importance in aromatic polymers with rigid chains.

9,9-Bis(4-aminophenyl)fluorene (**2n**) is one of the monomers with cardo groups. Polyamides with excellent solubility in organic solvents can be obtained from it by low-temperature (acceptor-catalytic) solution polycondensation with diacid chlorides such as terephthaloyl dichloride; however, its polypyromellitimide is insoluble in all common organic solvents due to the less polarity of fluorene unit compared to other cardo groups such as phthalide and phthalimide groups¹⁶⁾. In this article, diamine **2n** was first condensed with trimellitic anhydride, leading to the fluorene- and imide-ring-containing dicarboxylic acid **1**, which was directly polycondensated with various aromatic diamines by use of triphenyl phosphite and pyridine as condensing agents in NMP in the presence of calcium chloride, giving rise to polymers containing alternating (imide-imide)-(amide-amide) links in the polymer backbone together with pendant cyclic fluorene unit. Cardo poly(amide-imide)s with this type of molecular sequence have not yet been reported in literature. These polymers with bulky groups along the inherently thermally stable main chain are expected to exhibit excellent solubility in organic solvents while still maintaining high heat resistance. Their solubility, thermal properties, and tensile properties are investigated in this paper.

Experimental part

Materials: Trimellitic anhydride was used without previous purification. *p*-Phenylenediamine (**2a**) and *m*-phenylenediamine (**2b**) were vacuum-distilled before use. According to the reported method¹⁷⁾, 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (**2o**) was prepared starting from tetraphenylthiophene, which was easily obtained by the reaction of benzyl chloride with powdered sulfur at an elevated temperature. All other diamines **2c–n** were of high purity when received from the manufacturers and used without any further purification. Commercially obtained 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.

N,N'-(9-Fluorenylidenedi-1,4-phenylene)diphthalimide-4-carboxylic acid (**1**): 34,8 g (0,1 mol) of 9,9-bis(4-aminophenyl)fluorene and 38,4 g (0,2 mol) of trimellitic anhydride were heated in 250 mL of dry DMF to 60 °C for 1 h. About 100 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, about 20 mL of methanol was added and the precipitated diimide-diacid **1** (yield: 59,8 g (86%)) was isolated by filtration and recrystallized from DMF; yellow powder; m. p.: 330 °C.

C ₄₃ H ₂₄ N ₂ O ₈ (696,7)	Calc.	C 74,13	H 3,47	N 4,02
	Found	C 74,10	H 3,50	N 4,10

Polycondensation: A typical example of polycondensation was as follows. A mixture of 1,74 g (2,5 mmol) of diimide-diacid **1**, 0,50 g (2,5 mmol) of 4,4'-oxydianiline (**2e**), 1,6 g of calcium chloride, 1,61 g (5,2 mmol) of triphenyl phosphite, 4 mL of pyridine, and 16 mL of NMP was

heated with stirring at 105 °C for 3 h under nitrogen. The resulting polymer solution was trickled on 500 mL of methanol giving rise to a stringy, 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 was 0,99 dL/g, measured at a concentration of 0,5 g/dL in *N,N*-dimethylacetamide (DMAc) at 30 °C.

Other poly(amide-imide)s were synthesized analogously.

Measurements: Inherent viscosities of the poly(amide-imide)s were determined at 30 °C using 0,5 g/dL solutions in DMAc or NMP. A Canon-Fenske capillary viscometer was used without kinetic energy correction, since the solvent flow time exceeded 100 s.

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer.

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

Thermogravimetry (TG) was done on a Rigaku Thermoflex TG 8110 coupled to a Rigaku Thermal Analysis Station 100. Experiments were performed on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 20 °C/min.

DSC was performed 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 cm³/min).

Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger D-Max IIIa, using Ni-filtered CuK_α radiation (40 kV, 15 mA).

An Instron Universal Tester Model 1130 with a load cell 5 Kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature (about 20 °C) with film specimens (0,5 cm wide, 6 cm long, and about 0,1 mm thick), and an average of at least five individual determinations was used.

Results and discussion

Syntheses

N,N'-(9-Fluorenylidenedi-1,4-phenylene)diphthalimide-4-carboxylic acid (**1**) was prepared by condensation of 4,4'-(9-fluorenylidene)dianiline [9,9-bis(4-aminophenyl)fluorene (**2n**)] with trimellitic anhydride. Complete cyclization of the intermediate amic acid was achieved by toluene-water azeotropic distillation.

The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents has been known since 1975 to be a convenient method for the preparation of aromatic polyamides on a laboratory scale⁹). This method was applied here to prepare the fluorene-containing poly(amide-

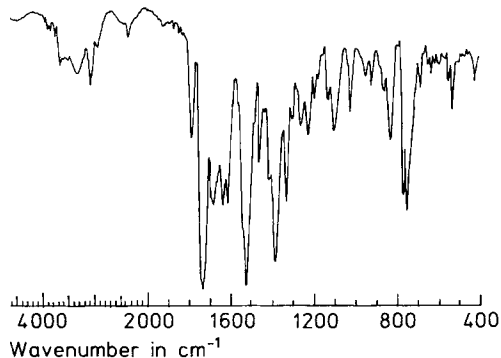
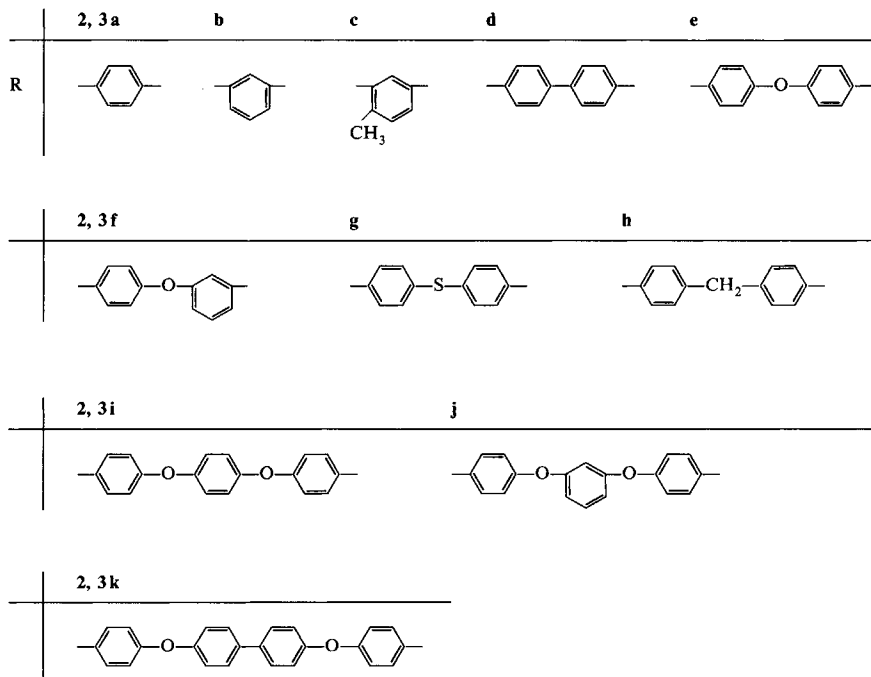
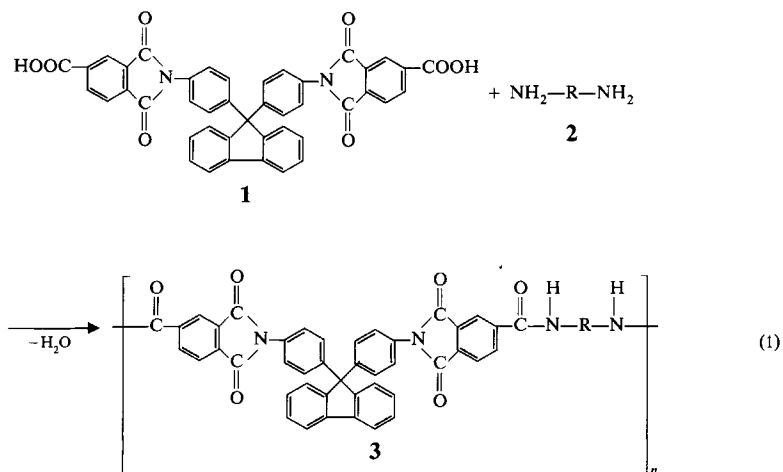
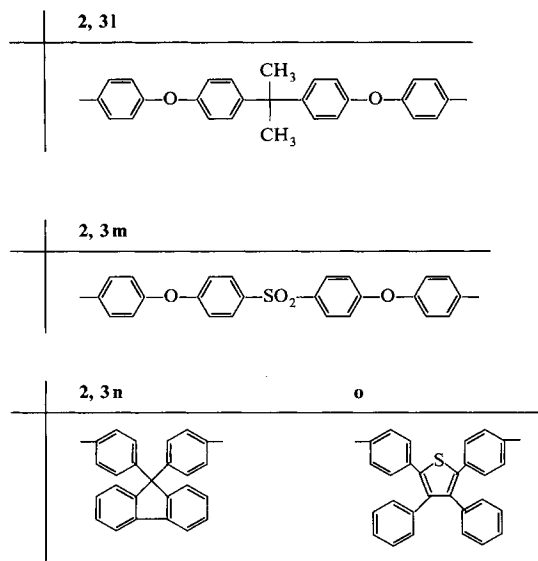


Fig. 1. IR spectrum of poly(amide-imide) **3n**

imide)s **3a–o** from diimidodicarboxylic acid **1** and structurally different aromatic diamines (**2a–o**) (Eq. (1)):

Scheme:





Almost all the reactions proceeded readily in homogeneous solution by using the conditions listed in Tab. 1. In some cases such as reactions of diacid **1** with diamines **2a**, **2d**, and **2o**, an additional volume of 8–16 mL of NMP (warmed, if necessary) was added to the reaction mixture after 15 min before precipitation or gelation took place after about 20 min. The results of the polycondensation are summarized in Tab. 1. The polycondensation reactions gave quantitative yields of poly(amide-imide)s with inherent viscosities ranging from 0,59–1,13 dL/g, indicating the formation of high-molecular-weight polymers.

The compositions and structures of these polymers were confirmed by their elemental analyses and IR spectra. Fig. 1 shows the typical IR spectrum of the representative poly(amide-imide) **3n**. The characteristic imide absorptions at 1780, 1710 and 740 cm^{-1} and the characteristic amide absorptions at 3300 cm^{-1} and 1680 cm^{-1} support the formation of the poly(amide-imide). The elemental analyses of the poly(amide-imide)s are listed in Tab. 2. In all cases the carbon values were found to be lower than the calculated ones for the proposed structures, and the hydrogen values were higher than the calculated ones. This can probably be explained by the hygroscopic nature of the samples caused by the amide groups of poly(amide-imide)s.

Properties of the polymers

The X-ray diffraction patterns of the fluorene-containing poly(amide-imide)s indicated that all the polymers were amorphous. The solubility behavior of the poly(amide-imide)s is shown in Tab. 2. These polymers were soluble in a variety of solvents such as DMF, DMAc, NMP, and DMSO, and even in *m*-cresol; however, polymer **3d** with biphenyl structure had somewhat limited solubility and was insoluble

Tab. 1. Inherent viscosities η_{inh} , yields and elemental analyses of poly(amide-imide)s^{a)}

Polymer	Yield in %	η_{inh}^b in dL/g	Formula (Mol. weight)	Elemental analysis			
				C	H	N	
3a	99	0,98	$(C_{49}H_{28}N_4O_6)_n$ (768,78) _n	Calc.	76,55	3,67	7,28
				Found	73,29	3,80	7,16
3b	99	0,69	$(C_{49}H_{28}N_4O_6)_n$ (768,78) _n	Calc.	76,55	3,67	7,28
				Found	74,22	3,82	7,33
3c	99	0,80	$(C_{50}H_{30}N_4O_6)_n$ (782,81) _n	Calc.	76,71	3,86	7,16
				Found	74,37	4,08	7,24
3d	96	0,98 ^{c)}	$(C_{55}H_{32}N_4O_6)_n$ (844,85) _n	Calc.	78,19	3,81	6,63
				Found	75,57	3,74	6,67
3e	99	0,99	$(C_{55}H_{32}N_4O_7)_n$ (860,88) _n	Calc.	76,74	3,74	6,51
				Found	74,36	3,99	6,49
3f	98	0,66	$(C_{55}H_{32}N_4O_7)_n$ (860,88) _n	Calc.	76,74	3,74	6,51
				Found	74,71	3,87	6,49
3g	99	0,72	$(C_{55}H_{32}N_4O_6S)_n$ (876,91) _n	Calc.	75,33	3,68	6,39
				Found	73,06	3,87	6,37
3h	99	0,81	$(C_{56}H_{34}N_4O_6)_n$ (858,91) _n	Calc.	78,31	3,99	6,52
				Found	76,20	4,03	6,26
3i	99	1,02	$(C_{61}H_{36}N_4O_8)_n$ (952,98) _n	Calc.	76,88	3,81	5,88
				Found	75,01	3,95	5,98
3j	99	0,71	$(C_{61}H_{36}N_4O_8)_n$ (952,98) _n	Calc.	76,88	3,81	5,88
				Found	75,13	3,89	5,76
3k	99	0,97	$(C_{67}H_{40}N_4O_8)_n$ (1 029,07) _n	Calc.	78,20	3,92	5,44
				Found	75,95	4,08	5,35
3l	98	0,90	$(C_{70}H_{46}N_4O_8)_n$ (1 071,15) _n	Calc.	78,49	4,33	5,23
				Found	75,01	4,50	5,21
3m	99	0,92	$(C_{67}H_{40}N_4O_{10}S)_n$ (1 093,13) _n	Calc.	73,61	3,69	5,12
				Found	71,82	3,77	5,19
3n	99	0,59	$(C_{68}H_{40}N_4O_6)_n$ (1 009, 08) _n	Calc.	80,94	3,99	5,55
				Found	78,84	4,14	5,61
3o	99	1,13 ^{c)}	$(C_{71}H_{32}N_4O_6S)_n$ (1 069,12) _n	Calc.	79,76	3,01	5,24
				Found	76,77	4,01	5,27

a) Polymerization was carried out using 2,5 mmol of diamine **2** and 2,5 mmol of diimidodiacid **1** with 5,2 mmol of triphenyl phosphite in 4 mL of pyridine and 16 mL of NMP containing 1,6 g of calcium chloride at 105 °C.

b) Measured at a concentration of 0,5 g/dL in DMAc at 30 °C.

c) Measured at a concentration of 0,5 g/dL in NMP at 30 °C.

in DMF, DMAc and DMSO, but soluble in NMP and *m*-cresol. All the polymers were practically insoluble in chloroform. Their high solubility and amorphous nature can be apparently attributed to the introduction of bulky fluorene units along the unsymmetrical trimellitimide-based poly(amide-imide) backbone.

Transparent, flexible, and tough films could be cast from the NMP solutions of polymers **3d** and **3o**, and from the DMAc solutions of the other polymers. The tensile properties of the poly(amide-imide) films are summarized in Tab. 3. The films had tensile strengths of 68–131 MPa, elongations to break of 6–43%, and initial moduli of 2,13–3,18 GPa.

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

Polymer	Solvent ^{b)}					
	DMF	DMAc	DMSO	NMP	<i>m</i> -Cresol	Chloroform
3a	+	+	- +	+	+	-
3b	+	+	+	+	+	-
3c	+	+	+	+	+	-
3d	-	-	-	+	+	-
3e	+	+	+	+	+	-
3f	+	+	+	+	+	-
3g	+	+	+	+	+	-
3h	+	+	+	+	+	-
3i	+	+	+	+	+	-
3j	+	+	+	+	+	-
3k	+	+	+	- +	+	-
3l	- +	+	+	+	+	-
3m	+	+	+	+	+	-
3n	+	+	+	+	+	-
3o	- +	- +	- +	+	+	-

a) +: soluble; - +: slightly soluble; -: insoluble.

b) DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; NMP: 1-methyl-2-pyrrolidone.

Tab. 3. Tensile properties of poly(amide-imide) films

Polymer	Strength at break in MPa	Elongation to break in %	Initial modulus in GPa
3a	94	16	2,50
3b	98	10	2,90
3c	105	13	2,33
3d	114	6	3,18
3e	91	10	2,63
3f	96	6	2,57
3g	96	14	2,61
3h	85	10	2,18
3i	115	43	2,45
3j	83	14	2,13
3k	91	13	2,39
3l	68	5	2,13
3m	85	12	2,29
3n	110	7	2,87
3o	131	7	3,03

The thermal properties of the polymers were evaluated by means of DSC and TG. Fig. 2 shows typical DSC and TG curves of poly(amide-imide) **3g**, and the thermal behavior data of all poly(amide-imide)s are summarized in Tab. 4. Dynamic TG data indicated that all the polymers possess excellent thermal stability, with no significant weight loss up to temperatures of approximately 500 °C in nitrogen, and their 10%

weight loss temperatures ranged from 532 to 622 °C in nitrogen. It should be noted that the amount of carbonized residue of the poly(amide-imide)s at 800 °C in nitrogen atmosphere was very high and reached up to 79%.

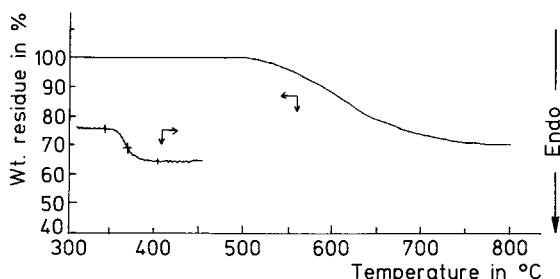


Fig. 2. DSC and TG curves for poly(amide-imide) **3g**; heating rate: 20 °C/min, in nitrogen

Tab. 4. Thermal behavior of poly(amide-imide)s

Polymer	DSC T_g / °C ^{b)}	TG ^{a)}			
		temperature (in °C) at various wt.-losses			residual wt.-% at 800 °C
		5%	10%	30%	
3a	No ^{c)}	530	575	782	69,7
3b	No	532	576	734	75,0
3c	No	558	626	775	69,6
3d	No	515	562	717	67,3
3e	383	571	599	—	79,2
3f	353	527	577	748	68,3
3g	365	546	590	—	72,8
3h	345	513	568	578	69,3
3i	347	526	574	794	69,9
3j	337	525	580	794	69,9
3k	362	525	580	758	68,7
3l	327	514	532	589	56,6
3m	367	519	562	696	66,9
3n	No	486	566	745	69,0
3o	No	472	558	—	70,0

- a) Thermogravimetry was conducted at a heating rate of 20 °C/min in nitrogen atmosphere.
 b) Glass transition temperature obtained as the mid-point of the change in slope on the second heating DSC trace obtained with a heating rate of 20 °C/min in nitrogen atmosphere.
 c) Not observed before decomposition.

The glass transition temperatures (T_g) of the poly(amide-imide)s were above 320 °C. Polymer **3l**, containing an aliphatic linkage in the main chain, showed the lowest T_g value (327 °C). T_g 's of the polymers can be controlled by varying the bridge group between the phenyl rings of the diamine residues. Polymers **3a–d**, containing structurally rigid 1,4-phenylene, 1,3-phenylene, 2,4-tolylene, and 4,4'-biphenylene

units, respectively, and polymers **3n** and **3o**, derived from highly phenylated, bulky diamines, had high T_g 's, which were not attained because of decomposition.

In conclusion, the introduction of bulky fluorene unit into the trimellitimide-based poly(amide-imide) backbone resulted in soluble poly(amide-imide)s with high T_g 's and high thermal stability. Thus, these poly(amide-imide)s are considered to be new, promising, processable, high-temperature-resistant polymer materials.

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