

Synthesis and Characterization of Novel Poly(amide imide)s

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SYNOPSIS

Novel poly(amide imide)s having inherent viscosities in the range 0.89–1.56 dL/g were prepared by the method of low temperature polycondensation in solution of *N,N*-dimethylacetamide (DMA) from aromatic diamines and a new monomer: *N*-[4'-(chloroformylphenyl)-4'-iminobenzoyl]trimellitimide chloride. The polymers were soluble in polar aprotic solvents and essentially amorphous. They showed glass transition temperatures in the range 310–350°C and decomposition temperatures of 450–460°C. Polymer films, fabricated by casting polymer solutions in DMA, showed tensile strengths in the range 70–90 MPa and moduli values between 3000–4000 MPa. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Imide polymers and copolymers are a well-established class of polymers that show a good combination of mechanical, electrical, and thermal properties.^{1,2} Since fully aromatic polyamides are intracastable materials that do not melt before thermally decomposing, and do not dissolve in any organic solvent, copolyimides were developed as a valuable alternative in the 1960s.^{3,4} Many attempts have been made since then to modify the chemical structure of polyimides and copolyimides, always with the aim of minimizing the shortcomings of aromatic polyimides while preserving their outstanding properties to the largest extent.^{5,6}

Poly(amide imide)s (PAIs), as a family, have deserved particular attention as they are probably the class of copolyimides that more closely resemble the thermal properties of aromatic polyimides. Many PAIs described so far are highly aromatic, yet soluble in some organic polar solvents. Examples of PAIs have been marketed as moldable materials in the melt at high temperature,⁷ so they are considered as thermoplastic polyimides.

This paper describes the synthesis and properties of aromatic PAIs prepared from aromatic diamines and *N*-[4'-(chloroformylphenyl)-4'-iminobenzoyl]trimellitimide chloride (TMI-BA), a new monomer

containing preformed amide and imide groups. Traditionally, PAIs have been described as linear polymers; but there is a real probability that those synthesized from anhydride monomers, via polyamic acid intermediates followed by thermal imidation, are partially crosslinked. The use of monomers containing preformed imide rings is one method of circumventing such a problem, because it avoids high-temperature curing cycles and handling unstable intermediates such as polyamic acids.^{8–13} Thus we designed the monomer TMI-BA with a preformed imide ring as an “enlarged” monomer containing an additional benzamide group, which also helps to achieve high molecular weight PAIs by conventional means at low temperature.

EXPERIMENTAL

Solvents and reagents were commercially available and were used as received unless otherwise indicated. *N,N*-Dimethylacetamide (DMA) and *N*-methyl-2-pyrrolidone (NMP) were distilled twice at reduced pressure over phosphorus pentoxide. Both solvents were then stored in sealed, dark flasks over molecular sieves. Lithium chloride was dried at 300°C for 15 h. The diamines 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylether (DDE), and 2,2-bis(4-aminophenyl)hexafluoropropane were used without further purification. *m*-Phenylenediamine (MPD) was purified by sublimation just before use.

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4-(4-Nitrobenzamido)benzoic acid (**1**) was synthesized by the reaction of equimolar amounts of 4-nitrobenzoic acid chloride and 4-aminobenzoic acid in tetrahydrofuran (THF) at 0°C. After 2 h, the precipitate that formed was filtered off and dried to yield yellow crystals with a melting point (mp) of 325°C (in literature, 326–327°C).¹⁴ Yield was 90%.

4-(4-Aminobenzamido)benzoic acid (**2**) was prepared by hydrogen reduction of **1** in an autoclave fitted with cradle stirring, under 3 atm pressure and room temperature, using 5% platinum/carbon as catalyst and DMA as solvent. The catalyst was removed by filtration and the product was precipitated on water, filtered off, washed, dried, and finally crystallized from ethanol-water, rendering white crystals, mp: 273°C, decomp., (in literature, 276°C, decomposed).¹⁴ Yield was 85%.

4-[(2,5-Dicarboxybenzamido)-4'-benzamido]-benzoic acid (**3**) was prepared by the reaction of equimolar amounts of **2** and trimellitic anhydride in THF at 50°C for 2 h. The reaction mixture was then concentrated and the precipitate that formed was filtered off and dried. It was used for the following step without further purification. Yield: 92%.

TMI-BA was synthesized by refluxing **3** with a 10-fold molar excess of thionyl chloride and a catalytic amount of *N,N*-dimethylformamide for 3 h. The excess of thionyl chloride was then rotary-distilled off, and the solid residue, recrystallized three times from toluene, was yellow crystals, mp: 220°C. Yield: 73%.

Polymer Synthesis

The general procedure consisted of adding, portionwise, 10.0 mmol of TMI-BA to a cooled (0°C) stirred solution of 10.0 mmol of diamine in 20 mL of DMA for polymers **4b–d** and of NMP containing 5% LiCl for polymer **4a**. After the reagents dissolved completely, 10.0 mmol of trimethylchlorosilane was added and the reaction was allowed to proceed for 2 h under a blanket of nitrogen. Then the temperature was raised to 20°C and the reaction proceeded for 2 h. The very viscous final solution was poured into distilled water and the polymer fibrous precipitate was filtered off, thoroughly washed with water, and finally dried in a vacuum oven at 90°C for 24 h. Yields over 95% were achieved.

Measurements

Viscosities were measured on 5% NMP solutions at 30.0 ± 0.1°C in an automated Ubbelohde viscometer.

¹H-NMR spectra were recorded on a Varian Unity 500 spectrometer at 499.843 MHz, using deuterated dimethylsulfoxide as solvent and tetramethylsilane as reference at 60°C under the following conditions: pulse angle, 90 degrees; acquisition time, 2 s; sweep width, 2366.4 Hz; and data size, 64,000.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies were performed with Perkin-Elmer devices DSC-7 and TGA-7, respectively. All samples were tested under nitrogen at a heating rate of 10°/min. Second-run curves of TGA were considered after a first run up to 250°C to eliminate absorbed water and small rests of solvent.

Wide angle X-ray diffraction (WAXD) patterns were obtained from polymer films at room temperature by using a Philips Geiger X-ray diffractometer, operating in the 2θ range between 2 and 32 degrees at a rate of 2°/min, using Ni-filtered CuKα radiation.

Polymer films were fabricated by casting of 6–8% solutions (w/v) in DMA or DMA/NMP mixtures on glass plates, and evaporating the solvent by heating for 5 h at 120°C in an air-circulating oven and then 24 h at 120°C in a vacuum oven. Solvent rests were removed by soaking the films in methanol at room temperature for 24 h and drying the films again in a vacuum oven at 80°C for 8 h. For the measurements of mechanical properties, strips of 5 × 80 mm were cut from polymer films and measured on an Instron 1122 dynamometer at 20°C. Pneumatic clamps were used, and an extension rate of 2 mm/min was applied, with a gauge length of 10 mm.

RESULTS AND DISCUSSION

Monomer and Polymers Synthesis and Characterization

Monomer TMI-BA was prepared by the synthetic route depicted in Figure 1.

The four-step synthetic route led to the monomer with acceptable yield. The most hazardous step was the last one because **3** had to be treated with thionyl chloride, and it is known that the HCl that evolves as side product during the acylation reaction can react with an amido group and decompose intermediate **3** through the von Braun reaction.¹⁵ In fact the breaking out of the amido group of **3** should occur in some extension as the yield of the acylation was only 73%; yet the monomer could be isolated and crystallized up to the purity degree required for polycondensation.

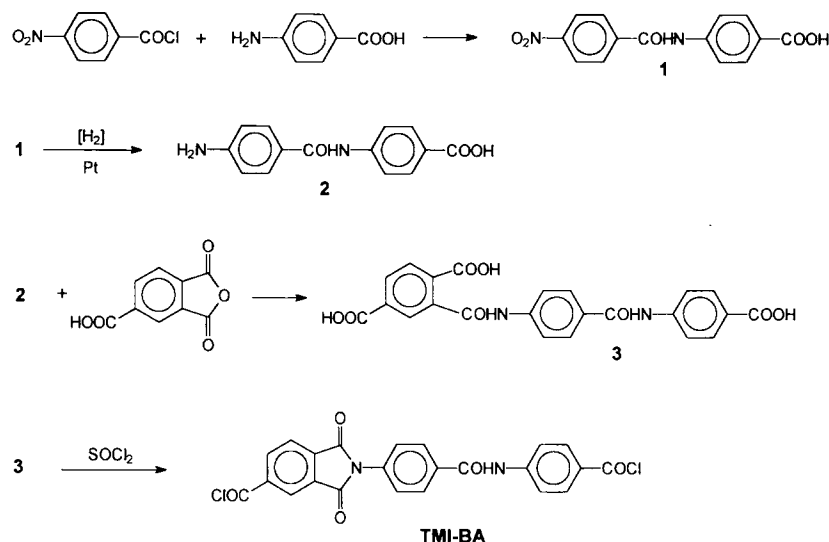


Figure 1 Synthetic route for monomer TMI-BA.

Polymers were prepared by the traditional method of low-temperature polycondensation in a solution of DMA. Monomer TMI-BA was soluble in DMA at 0°C so the monomers and polymers remained dissolved all along the reaction; only incipient gelation took place at the end of the reaction for polymer **4a** even using the system NMP + LiCl as solvent. Trimethylchlorosilane was always used to improve yields and polymerization degree.¹⁶ Once isolated, polymers were characterized by conventional means. The general polycondensation reaction is depicted in Figure 2, and Table I shows the results of the synthesis along with elemental analysis and inherent viscosities.

The polymers structure was also confirmed by ¹H-NMR spectroscopy. As an example, the spectrum of polymer **4c** has been reproduced in Figure 3. The peaks corresponding to the three different amide groups present in the repeating unit appeared as three singlets at 10.58, 10.65, and 11.13 ppm for that polymer, and could be observed separately in the range 10.2–11.4 ppm in the ¹H-NMR spectra of the

set of polymers. Signals of impurities or peaks attributable to final groups were negligible or virtually undetectable in every case.

The inherent viscosity values listed in Table I speak for high-molecular-weight polymers, which is consistent with the fact that tough films could be obtained from polymer solutions by casting and elimination of the solvent. These results allowed us to confirm that monomer TMI-BA is very suitable for the preparation of PAIs and to presume that the character of *enlarged* monomer of TMI-BA did help in the attainment of high-molecular-weight polymers.

Polymer Properties

Improving the solubility of highly aromatic polymers is a major goal of many investigations, and it was also a priority in the present work. The solubility of the current PAIs can be considered as moderated, but they can be seen as quite soluble polymer materials if the usual insolubility of aromatic poly-

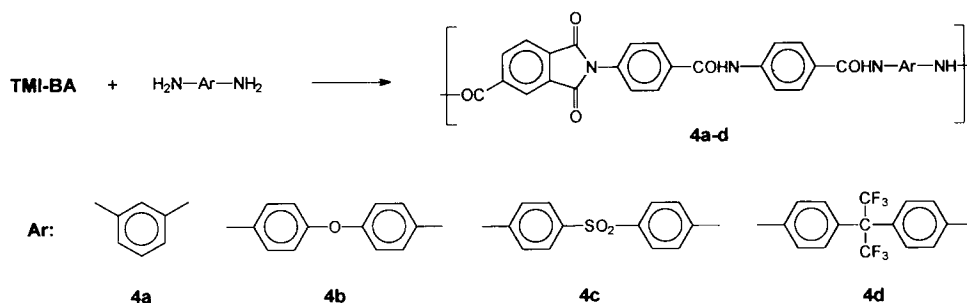


Figure 2 Synthesis of poly(amide imide)s.

Table I PAIs from TMI-BA

Polymer	Yield (%)	η_{inh} (dL/g)	Elemental Analysis					
			C (%)		H (%)		N (%)	
			Calc.	Found	Calc.	Found	Calc.	Found
4a	96	0.89	69.32	69.72	3.61	3.56	11.15	11.34
4b	95	1.70	70.70	71.01	3.73	3.85	9.42	9.80
4c	98	1.07	65.42	64.95	3.45	3.62	8.72	8.45
4d	98	1.56	62.64	62.55	3.04	3.12	7.69	7.80

amides and polyimides is borne in mind. They were soluble in aprotic polar solvents such as DMA, NMP, or DMSO, or mixtures of them, at concentrations high enough (6–8%) to fabricate films. The technical PAI Torlon[®] (General Electric), for instance, is less soluble than those reported here. The solubility, on the other hand, depends greatly on the diamine moiety, following the expected trend **4d** > **4c** > **4a** > **4b**.

Thermal properties were studied by DSC and programmed TGA. DSC and TGA data are listed in Table II. The values of T_g always correspond to the second run. Because of the high concentration of amide linkages, the current polymers showed a remarkable ability to take up water, and a wide endotherm assignable to water-splitting was observed

in the first run in the range 90–220°C. Thus a first curve was always run up to 300°C and, immediately afterwards, a second curve was recorded up to 400°C to measure the T_g . As expected all the polymers showed high T_g s, in the range 310–350°C. The PAI from MPD showed the highest T_g , and polymer **4b**, from DDE, showed the lowest one.

A melting endotherm was never observed within the temperature range scanned by DSC. It may be assumed that the polymers' melting temperature lies above 400°C, or even beyond the decomposition temperature. But the absence of a melting endotherm must rather be attributed to the essentially amorphous character of the PAIs. In fact, no reflexion peak due to three dimensions order could be observed by WAXD, and only the usual amorphous

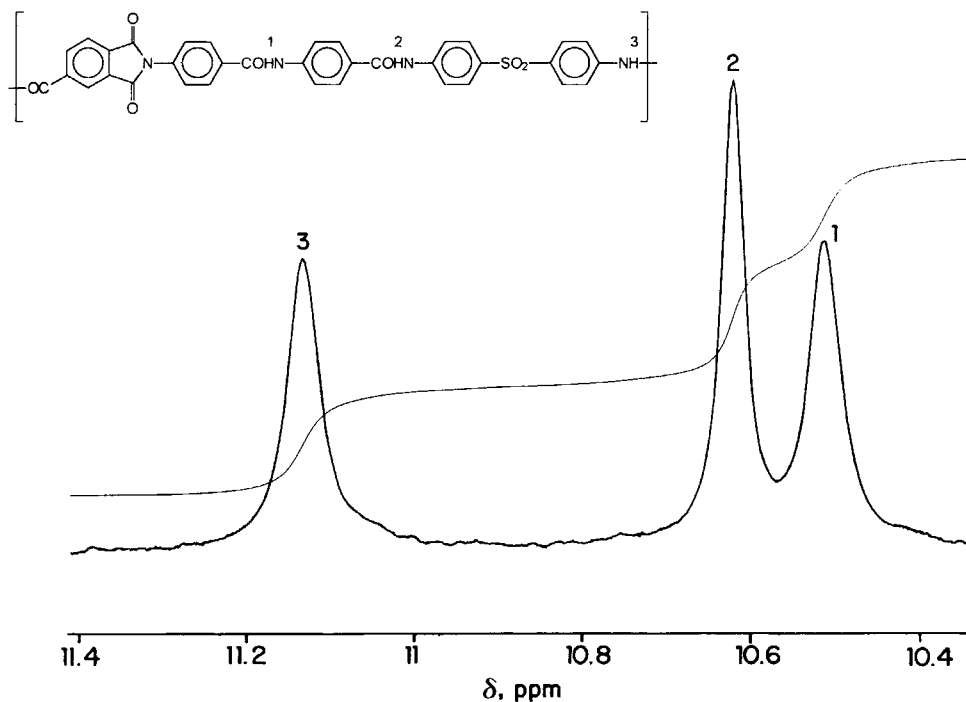
Figure 3 ¹H-NMR spectrum (NH region) of polymer 4c.

Table II Properties of PAIS from TMI-BA

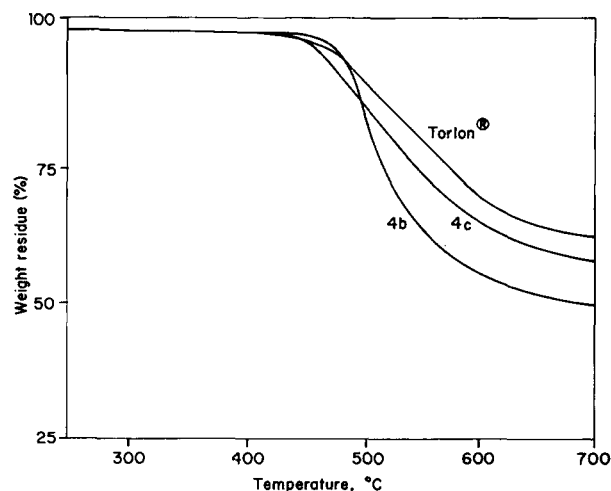
Polymer	Solubility ^a		T_g	T_d	R_{700} (%)
	DMA	<i>m</i> -Cresol			
4a	++	±	344	460	54
4b	+	-	310	460	50
4c	++	+	334	450	60
4d	++	++	325	445	50
Torlon TM	±	±	275 ^b	455	64

^a ++: soluble at room temperature; +: soluble in hot; ±: partially soluble; -: insoluble.

^b Deflection temperature (1.8 MPa)⁷.

“halo” of noncrystalline polymers was recorded in every case.

The values of T_d (initial decomposition temperature by TGA) were taken as the onset temperature when the fastest weight-loss process begins. These values reasonably agree with values of T_d when the criterion is the temperature of 5–10% weight loss. However, for highly hygroscopic and highly polar polymers, as is the case of the current PAIs, the onset-temperature method is more convenient because a weight-loss step is observed at low temperatures associated with the loss of moisture absorbed and/or with the escaping of entrapped solvent. Examples of the TGA curves are reproduced in Figure 4, which shows that the thermal resistance of the current PAIs is comparable to that of the commercial reference. T_d s in the range 445–460°C and weight residues at 700°C (nitrogen) over 50% clearly qualify these polymers as thermally stable. The weight retention at high temperature (700°C) is higher for the technical PAI, most probably due to its higher

**Figure 4** TGA curves of PAIs (nitrogen, 10°/min).**Table III** Mechanical Properties of PAIs from TMI-BA

Polymer	Tensile Strength (MPa)	Elongation (%)	Modulus (MPa)
4a	92	3.5	4200
4b	86	3.6	3300
4c	73	4.5	3000
4d	82	2.5	3200

content of imide units. On the other hand, these data compare well with data previously reported on the thermal stability of fully aromatic PAIs.^{6,10,17,18}

Mechanical properties were measured on polymer films made by the casting of polymer solutions and solvent evaporation. The films were yellowish, tough, and creasable, and were tested for tensile strength, tensile modulus, and elongation at break. For thin films (70–100 μm), deviations as large as $\pm 12\%$ for moduli and $\pm 5\%$ for tensile strengths were measured, so eight to ten specimens were used for each polymer. The averaged data have been collected in Table III.

Although differences could be partially attributed to the different viscosity of the polymers, the wholly aromatic polymer 4a had the best mechanical resistance and modulus in spite of its lower viscosity. The values compare fairly well with the values of tensile strength and modulus of experimental aromatic polyamides and copolyimides previously reported, although the value of tensile strength was expectedly lower than that of the technical PAI Torlon.⁷

CONCLUSIONS

Monomer TMI-BA, containing preformed amide and imide groups, is a suitable condensation monomer for the preparation of high molecular weight PAIs. These polymers show comparatively good solubility and are essentially amorphous.

The thermal and mechanical properties of the set of PAIs reported here compare well with those of related technical polymers, and because of their high T_g s and thermal resistance they can be considered as thermally stable polymer materials.

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