

Crosslinkable Polyamide-Imides

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Synopsis

A series of polyamide-imides were prepared from aromatic diamines and substituted isophthaloyl chlorides containing unsaturated imide rings. Aromatic polyamides from isophthaloyl chloride were also prepared for comparison. The polyamide-imides gave enhanced solubility compared to the aromatic polyamides and there was no deterioration in thermal stability or T_g . The PAIs were crosslinked by heating at 280°C/4 h under nitrogen. After this heat treatment all the PAIs became insoluble and their mechanical properties increased substantially; their thermal behavior, as measured by DSC and TGA, changed as a function of their chemical structure.

INTRODUCTION

Aromatic polyimides have reached universal acceptance as high-performance polymers because of their outstanding thermal stability. However, their utilization is greatly restricted by poor handling and processing characteristics. Polyamide-imides and polyester-imides were first developed as alternative materials, which, without much deterioration in thermal properties, provided better processability.^{1,2} More recently, addition polyimides have emerged as a promising approach in the preparation of polyimides with improved processability.³ Addition polyimides are generally based on soluble oligomers endcapped with latent crosslinking groups, such as maleimide,^{4,5} nadimide,⁶⁻⁸ or acetylene groups.^{9,10} They are easily applied, and the final cure is normally carried out under pressure and at moderately high temperature, thus giving rise to insoluble 3-dimensional structures with very good thermal and mechanical properties.

The aim of the present work was to obtain aromatic polyamides with reactive imide groups as pendent substituents. We had observed previously that the introduction of side imide rings is a good method of enhancing the solubility of aromatic polyamides without loss of thermal resistance.¹¹ The possibility of having soluble polyamide-imides which can be eventually cured by means of olefinic side groups may be an easy method to prepare new heat-resistant polymers with attractive properties, and examples of them are actually found in the patent literature.^{12,13}

EXPERIMENTAL

Materials and Monomers

5-Aminoisophthalic acid and the anhydrides of the acids maleic, tetrahydrophthalic and nadic (5-norbornene-2,3-dicarboxylic), were obtained commercially and used without further purification. The solvent

N,N-dimethylacetamide (DMA) was purified as reported.¹¹ Isophthaloyl chloride was prepared by reaction of isophthalic acid and thionyl chloride and purified by recrystallization from *n*-hexane. Commercial bis(4-aminophenyl)methane was recrystallized from dry toluene under nitrogen. 2,2-Bis(4-aminophenyl)propane was prepared from aniline hydrochloride and acetone according to Ref. 14 and purified by recrystallization from water under nitrogen, mp 133°C (lit. 132°C).¹⁴

5-Imidoisophthalic acids were synthesized by condensation of 5-aminoisophthalic acid and the corresponding anhydride by the method previously described.¹¹ The 5-imidoisophthaloyl chlorides were prepared from them by treatment with thionyl chloride, and purified by recrystallization from *n*-hexane or *n*-heptane. They had the following melting points (unc.): 5-maleimidoisophthaloyl chloride, 112°C; 5-tetrahydrophthalimidoisophthaloyl chloride, 96°C; 5-nadimidoisophthaloyl chloride, 164°C.

Polycondensations

All polycondensations were conducted in DMA at low temperature. In a typical example 2.6202 g (0.0116 mol) of 2,2-bis(4-aminophenyl)propane were dissolved in 30 mL of DMA in a polycondensation flask fitted with stirrer and nitrogen inlet and outlet. The solution was cooled to -5°C and 3.4506 g (0.0116 mol) of 5-maleimidoisophthaloyl chloride was added in several portions. The temperature was then allowed to rise to room temperature, and the reaction continued for 1 h. The viscous solution was cooled to 0°C and 5 mL (ca. 0.07 mol) of propylene oxide was added, causing an apparent further increase in solubility. The solution was diluted with two volumes of DMA, and then the polymer was isolated by precipitation on distilled water, filtered off, thoroughly washed with water, extracted with acetone in a Soxhlet apparatus, and dried in a vacuum oven at 60°C, yield 97%: η_{inh} : 0.67 dL/g (0.5% in NMP, 25°C).

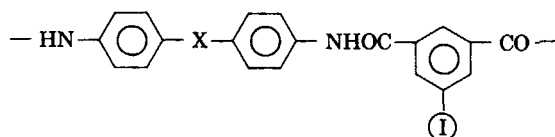
ANAL. (REPEATING UNIT). Calcd for $C_{27}H_{21}N_3O_4$ (451.51): C, 71.84%; H, 4.66%; N, 9.31%. Found: C, 70.87%; H, 4.35%; N, 9.12%.

IR (cm^{-1}): 3325(ν_{N-H}), 1780 and 1725 (symm. and asymm. $\nu_{C=O}$ imide), 1600($\nu_{C=O}$ amide), 1530(ν_{C-N} and δ_{N-H} amide), 840(δ_{C-H} maleimide). 1H -NMR δ (ppm): 10.45(s, 2H), 8.55(s, 2H), 8.10(s, 2H), 7.70(d, 4H), 7.25(d, 4H), 7.20(s, 2H), 1.70(s, 6H).

Characterization and Measurements

The elemental analyses were carried out by the Microanalysis Service of the CNQO (Madrid). The IR spectra were recorded with a Perkin-Elmer 457 Spectrophotometer on thin polymer films. The 1H -NMR spectra were recorded at 90°C on a Varian EM-390 (90 MHz) spectrometer, using dimethylsulfoxide- d_6 as solvent and hexamethyldisiloxane as internal reference.

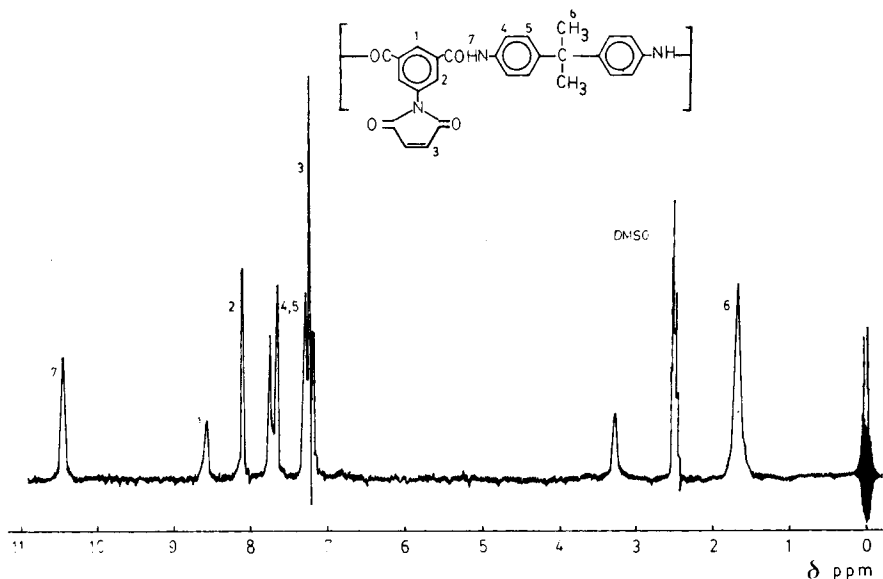
The viscosities were measured in a 0.4 mm i.d. Ostwald viscometer at $25.0 \pm 0.1^\circ C$ and 0.5 w/v polymer concentration. The thermogravimetric analyses were conducted in a Perkin-Elmer TGS-2 Thermobalance programmed by means of a System 4 Microprocessor. The decomposition temperature was defined as the temperature at which the onset of weight loss takes place in the TGA curve. The glass-transition temperatures were determined with a Perkin-Elmer DSC-4 system linked to a Data Station. All

TABLE I
 Polyamides and Polyamide-imides


Code	X	(I)	Yield (%)	η_{inh} (dL/g)	δ_{ppm}^a
1a	CH ₂	—	98	1.55	—
1b	CH ₂		96	0.94	7.2
1c	CH ₂		92	0.98	6.0
1d	CH ₂		98	0.78	6.2
2a	C(CH ₃) ₂	—	97	1.06	—
2b	C(CH ₃) ₂		97	0.67	7.2
2c	C(CH ₃) ₂		98	0.94	6.1
2d	C(CH ₃) ₂		95	0.65	6.2

^a Chemical shift of ethylenic protons.

polyamides: poly(4,4'-methylenediphenylene isophthalamide) and poly(4,4'-isopropylidenediphenylene isophthalamide), which we will refer to as PMDPIPA and PPDPIPA, respectively. The latter was soluble in polar solvents such as DMA, DMSO, and NMP as well as in hot cyclohexanone, and deviations from this behavior were not noted in PAIs with bis(4-phenyl) propane units, except that containing nadimide side groups, which is soluble in cyclohexanone at room temperature. Solubility changes were more readily observed in the case of PAIs containing bis(4-phenyl) methane moieties. The reference polyamide of this series, PMDPIPA, was insoluble in *m*-cresol and cyclohexanone while the PAIs derived from it were soluble in hot *m*-cresol, and the polymers with nadimide and tetrahydrophthalimide pendent

Fig. 1. $^1\text{H-NMR}$ spectrum of the polyamide-imide 2b.

groups were partially soluble even in hot cyclohexanone. Thus, imides as side substituents constituted, as a rule, a factor of asymmetry and steric hindrance that prevented a closer packing of the macromolecular chains which in turn resulted in a better solubility.

The enhancement of solubility of an aromatic polymer caused by structural modification generally brings about a decrease of the transition temperatures and heat resistance at the same time. However, in the investigation of the thermal behavior of the current polymers by DSC, we found that they did not follow this general rule. On the contrary, the presence of imide side groups had the effect of increasing the T_g , an effect more pronounced in the case of the voluminous imides, nadimide and tetrahy-

TABLE II
Properties of Polyamides and Polyamide-imides^a

Polymer	Solubility			T_g (°C)	T_m (°C)	T_d^c (°C)	Tensile strength (kg/cm ²)	Tensile strength after heat trtmt.
	DMA	<i>m</i> -Cresol	CH-one ^b					
1a	††	—	—	264	416	450	1040	1200
1b	††	†	—	287		450	830	1110
1c	††	†	±	286		455	700	850
1d	††	†	†	293		(240)450	720	950
2a	††	††	†	279	424	430	960	1060
2b	††	††	†	303		430	850	1020
2c	††	††	††	308		430	670	770
2d	††	††	†	311		(240)440	670	900

^a †† = soluble at room temperature, † = soluble by heating, ± = partially soluble or swelling, — = insoluble.

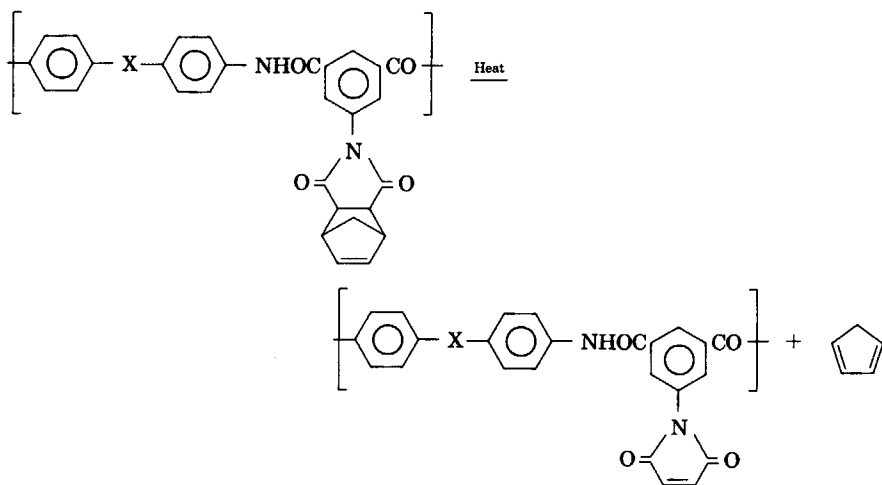
^b Cyclohexanone.

^c The temperature at which the Diels-Alder adduct decomposes is given in brackets.

drophthalimide, than with maleimide. The T_g increase was about 30°C for the former and only 10–20°C for the latter. This means that the pendent imides improved the performances of aromatic polyamides inasmuch as the better manageability (better solubility) not only did not reduce the glass transition temperatures but actually increased them by ca. 10–30°C.

Furthermore, the thermal resistance of PAIs measured by TGA compared well with that of the unsubstituted polyamides. It could also be observed that polymers 1a–1d had decomposition temperatures slightly higher than polymers 2a–2d; a higher concentration of aliphatic C—H linkages being the probable cause for the lower thermal resistance of polymers in the series 2. These results agree with previous studies on the heat stability of aromatic polyimides.^{15,16}

It is noteworthy that the TGA curves of PAIs with nadimide pendent groups showed two onsets of weight loss, the first one at about 240°C corresponding to the loss of cyclopentadiene by a thermal retro-Diels-Alder reaction:



The weight loss of nadimide polymers in the range 240–320°C almost quantitatively corresponded to a cyclopentadiene molecule per repeating unit, which means that cyclopentadiene escaped from the polymeric matrix and did not polymerize. Accordingly, the polymer should behave subsequently as the PAI of maleimide does, and this is the case (see Fig. 2). The conditions under which the thermogravimetric analyses were conducted (a few milligrams of sample and continuous N_2 flow) permitted the complete or practically complete removal of the diene.

A conscientious study of this reaction has been reported by Scola and Stevens on aliphatic and aromatic bisnadimides.⁸ From their results it can be stated that in the cure of nadimide-terminated polyimides retention of cyclopentadiene is never complete, and only under pressure can it be forced to copolymerize to any great extent.

Films of all the polymers could be obtained from concd. DMF or DMF/NMP solutions. The films were transparent, colorless to clear amber, and strong and flexible. Removal of solvent was not always complete even after

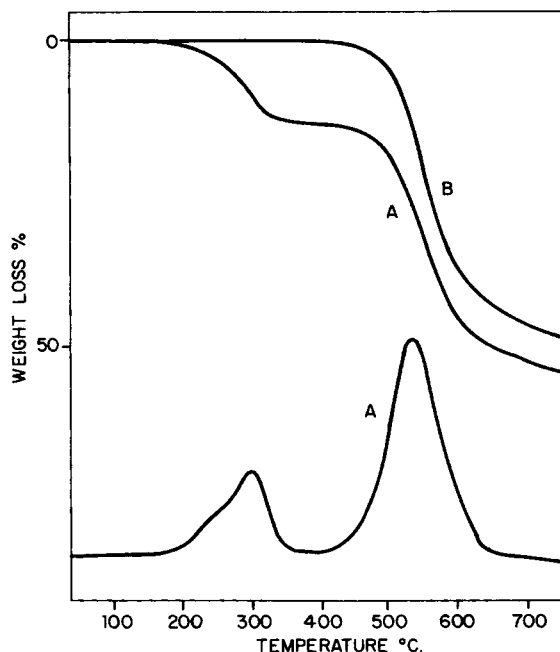


Fig. 2. TGA of polyamide 2d with nadimide pendent groups: (A) before heat treatment; (B) after heat treatment; (A') derivative curve of A.

heating at 200°C under vacuum, and up to 7–8% of entrapped solvent was observable when films were tested by TGA. Their tensile strengths are listed in Table II. The chemical structure predictably influenced the mechanical characteristics, and the differences can be related to the kind of diamine or imide-diacid used in the synthesis. Polymers with bis(4-phenyl)propane linkages in the main chain had tensile strengths somewhat lower than polymers with bis(4-phenyl)methane linkages, in analogy with the results on thermal resistance. The previously mentioned effect of sterical hindrance, more pronounced in the case of voluminous imides, which enhances the solubility of PAIs, had a negative influence on the tensile properties, so that the tensile strengths of PAIs with pendant nadimide and tetrahydrophthalimide displayed lower mechanical strengths than the parent polyamides.

Crosslinking and Crosslinking Effects

Thermal crosslinking of unsaturated polyimides can be conducted in practice under a variety of conditions depending on the nature of the imide.¹⁷ It has been reported that nadimide and maleimide end-capped oligomers readily polymerize at temperatures over 250°C in reasonably short times, while tetrahydrophthalimide, because of its more stable unstrained ring, reacts more slowly under the same conditions.⁸

In order to crosslink the PAIs synthesized in this work, polymer films samples were heated to 280°C for 4 h under nitrogen. Although some PAIs have T_g (transition midpoints) a little over this temperature, the transition onsets began at lower temperature in every case, and therefore the limit

of 280°C was taken as a compromise to prevent thermal decomposition while ensuring crosslinking. Films of the parent polyamides were also heated under the same conditions for comparison. The PAIs became insoluble in DMF, DMSO, and NMP, while PMDPIPA and PPDPIPA remained soluble. Thus, the latent crosslinking groups reacted at high temperature, and the extent of the reaction was enough to make the PAI films insoluble even in the case of tetrahydrophthalimide.

Exotherms corresponding to the crosslinking reaction appeared in the DSC traces (Fig. 3) after the T_g inflection and up to the start of polymer decomposition (440°C as determined by thermogravimetry at the same heating rate). At this temperature, the baseline had not yet been recovered in most cases, so that the last steps of crosslinking overlap with the initial thermal degradation, and that makes the accurate measurement of the enthalpy involved in the crosslinking exotherm impossible. In a second run, transitions in the DSC curves were no longer detected. This confirmed that the crosslinking reaction had progressed to such a degree as to immobilize the polymer chains within a three dimensional network.

In the case of PAIs with nadimide pendent groups, the crosslinking exotherms also overlapped with the endotherms corresponding to the loss of cyclopentadiene, whose maximum loss rate occurs at about 300°C, as can be seen by thermogravimetric analysis (Fig. 2). As a consequence, the T_g 's observed for these polymers should be taken as approximate inasmuch as the loss of cyclopentadiene is not complete at that temperature. That means that the observed glass transition temperatures of nadimide PAIs may correspond to copolymers nadimide-maleimide.

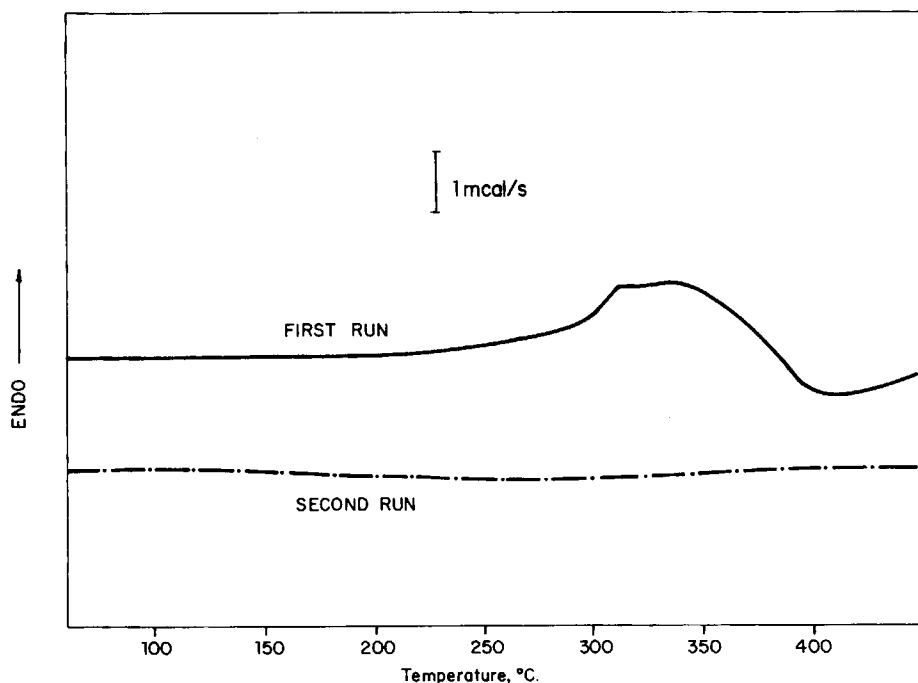


Fig. 3. DSC traces of polymer 1d.

TGA did not show substantial modifications of the initial decomposition temperatures after crosslinking; only the thermograms of PAIs with nadimide pendent groups became clearly different, the first weight loss in the range 240–320°C disappearing and the TGA curves for all the heated polymers becoming almost identical.

Changes in the mechanical properties were also observed. While the tensile strengths of the two unsubstituted polyamides were very similar before and after heating (a slight improvement being imputable to the loss of solvent residue after the energetic heat treatment, and not to an increase in molecular weight as the η_{inh} did not change after heating), substantial increases were measured for PAIs with nadimide and maleimide pendent groups, the magnitude of the change being lower for polymers 1d and 2d with tetrahydrophthalimide pendent groups. These results agree with predictions based on the reactivity of the three different imides.

However, the enhancement in mechanical properties cannot be taken quantitatively since some solvent retention was observed in PAI films before crosslinking, and the improvement in mechanical strength might be attributed in part to the complete removal of solvent at 280°C. Nevertheless, it should not have been large as demonstrated by the smaller change in the mechanical properties of unsubstituted polyamides after heat treatment.

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