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SYNTHESIS AND PROPERTIES OF NOVEL AROMATIC POLYAMIDES HAVING PENDANT *N,N′*-DIPHENYL IMIDE GROUPS

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ABSTRACT

We have investigated a novel monomer having two pendant phenyl imido groups for preparing new aromatic polyamides. Novel polyamides were synthesized by direct polycondensation reaction with the *N,N′*-diphenyl-2,3,5,6-diimido benzene-1,4-dicarboxylic acid chloride (PIBAC) and some aromatic diamines such as *p*-phenylene diamine, 4,4′-oxydianiline and 4,4′-methylene dianiline.

Inherent viscosity of the resulting polyamides are in the range 0.20-0.85 dl/g range. The decomposition temperature of these polyamides are ranged from 350-450°C and the ash contents of them orders MDA > ODA > SDA according to the kinds of the diamines used. In addition, the solubility of these polyamides is very good in aprotic solvents such as DMAc, NMP, and DMF. A transparent flexible and tough film was cast.

Key Words: Aromatic polyamide; Pendant imide group.

INTRODUCTION

Aromatic polyamides are known as the class of high performance heat resistance materials [1, 2]. Poly-*p*-phenyleneterephtalamide and poly-*m*-phenyleneiso-

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phtalamide, commercially known as Kevlar and Nomex, respectively, are composed of a phenylene unit and with an amide group and show ultra high-strength/high modulus properties. These polyamides exhibit a number of useful properties such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties. However, the poor solubility and high softening or melting temperature caused by high crystallinity and high stiffness of a polymer backbone lead to difficult processiblity of these aromatic polyamides.

In order to improve solubility, flexible groups such as 4,4′-oxydiphenylene, 4,4′-thiodiphenylene and 4,4′-sulfonyldiphenylene groups into a polymer chain [3, 4]. Conventionally, it is more convenient to synthesize the modified aromatic polyamides from the incorporation of flexible moiety into the diamine monomers, followed by the polycondensation reaction of them with dicarboxylic acids and their derivatives. In addition to the popular ether linkage-containing diamines of 4,4′-oxydianiline and 3,4-oxydianiline, there are also many aromatic diamine monomers which contain an additional ether linkage, such as 1,4-bis(4-aminophenoxy)benzene and 1,3-bis(4-aminophenoxy)benzene, which have been employed in the synthesis of aromatic polyamides [5, 6].

Several studies of the preparation of a polyamide with a naphthalene ring have appeared in the literature [7-13]. The introduction of a naphthalene ring into the polymer main chain is expected to lead to an increase in thermal stability in comparision to that with a benzene ring, because of the contribution from the more rigid structure of the former. Vinogradova *et al*. demonstrated that the polymer chain, having a cyclic side cardo group, e.g., a fluorene, a phthalamide, or a phthalimide group, can cause a significant increase in both glass transition temperature and thermal stability while providing good solubility [14, 15]. Y. Imai *et al*. reported aromatic polyamides having tetraphenyl-thiophene, and tetraphenyl furan units in their polymer backbones.

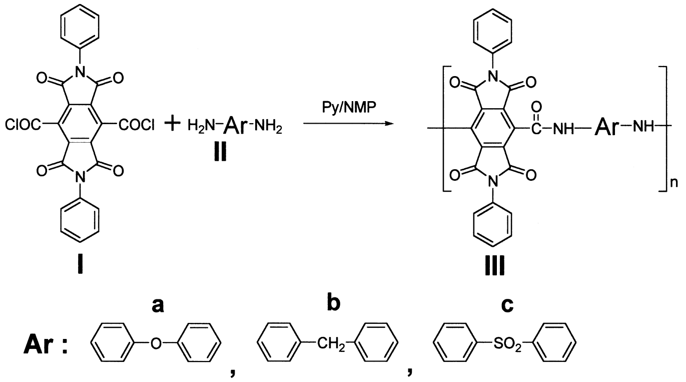
They mentioned that their aromatic polyamides had good solubility and high thermal stability, and had a high glass transition temperature above 300°C, since that pendant phenyl groups would allow increasing solubility while maintaining chain rigidity [16, 17].

Here, we report synthesis and characterization of new aromatic polyamides from a new monomer, *N,N′*-diphenyl-2,3,5,6-diimido benzene-1,4,-dicarboxylic acid(PIBAC), expecting that two pendant *N*-phenyl groups effectively give an increase in solubility to aromatic polyamides, and occasionally retains good thermal stability of these aromatic polyamides (Scheme 1).

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich, Junsei, and Merck Chemical Companies. 4,4′-sulfonedianiline (SDA) were purified by a vacuum sublimation



Scheme 1. Synthesis of polymers.

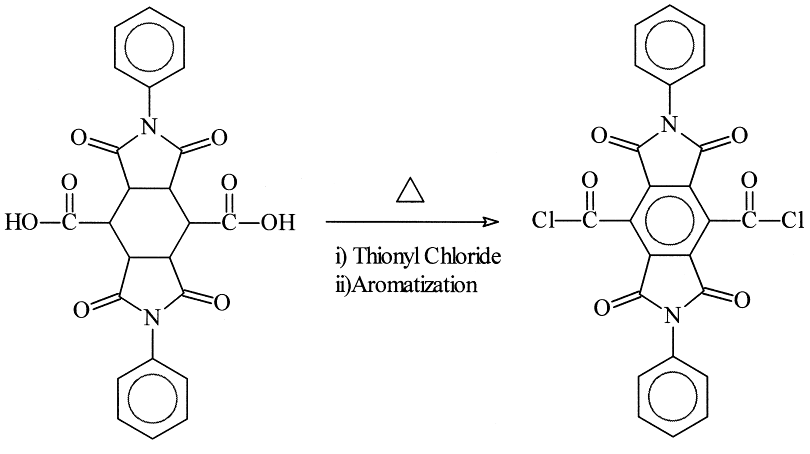
method. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150°C for 6 hours and 180°C for 10 hours. *N*-methyl-2-pyrrolidone (NMP) and pyridine purchased from (Aldrich Co.) were purified twice by distillation under reduced pressure over calcium hydride and stored over molecular sieve (4 Å). Pyridine was refluxed with KOH overnight, distilled at atmospheric pressure, and stored over molecular sieves (4 Å). In addition, pyridine was refluxed with KOH overnight, distilled at atmospheric pressure and stored over molecular sieves (4 Å).

Characterization and Equipment

^{1}H-NMR and ^{13}C-NMR spectra were obtained by a Brücker AMX300 in DMSO-d_6 or Acetone-d_6. FT-IR spectra were taken on a Bio-Rad Digi Lab. Division FTS-165 using a potassium bromide pellet. Elemental analysis was done on a EA 1108 Fisons. Differential Scanning Calorimetery (DSC) was conducted on a TA Instruments Dupont Model 910 at a heating rate of 10°C/min. under nitrogen. Thermogravimetric analysis (TGA) was performed with a TA Instruments Dupont Model 951 at a heating rate of 10°C/min. under nitrogen. Mass spectra was recorded on a Jeol JMS-DX 303 GC/MS system using an electron impact method. Gel permeation chromatography (GPC) was conducted with a water Model 150C using m-styragel columns with DMF as an eluent solvent. The viscosities were measured in a 0.4mm (i.d.) Ostwald viscometer at 30.0 ± 0.1°C with a 0.5g/dL polymer concentration in DMAc. The crystallinity of the polymers was examined by X-ray diffraction, diagrams were obtained using the powder method using nickel-filtered Cu K_a radiation.

N,N′-Diphenyl-2,3,5,6-diimido Benzene-1,4,-dicarboxylic Acid (PIBAC)

It was synthesized according to the previous method [18]. PIBAC was synthesized from a new method through an aromatization process. PICA reacts on



Scheme 2. Synthesis of *N,N*-diphenyl-2,3,5,6-diimide benzene-1,4-dicarbonylchloride (PIBAC).

Thionyl chloride with small amounts of Dimethyl acetamide as an activating agent. A mixture of PICA and Thionyl Chloride solutions was stirred at reflux condition for 12 hours, then the solution was cooled to room temperature giving a yellowish precipitation. The product was recrystallized in a chloroform solution. The yield of PIBAC was 85wt% (Scheme 2).

Polymerization

A mixture of 0.492 g (1 mmol) of PIBAC, 0.2 g (1 mmol) of ODA, 1 ml of pyridine, and 2 ml NMP was stirred at room temperature for 30 minutes, then the solution was heated to 70°C for 2 hours. The obtained polymer solution was addeded dropwise into 100 ml of methanol, thereby giving the yellowish precipitate which was washed thoroughly with methanol, hot water, and dried. The polyamides were purified again in the boiling methanol solution. The yield was quantitative. The inherent viscosity of polymer was 0.8 dl/g, measured at a 0.5g/dl concentration in DMAc at 30°C.

RESULTS AND DISCUSSION

Synthesis of Polymers

Wholly aromatic polyamides of high molecular weight were developed by various works at Dupont in the 1960's using low-temperature polycondensation with diacid chlorides and diamines [19-24]. In our system, this method was used because this polymerization method was a simple one.

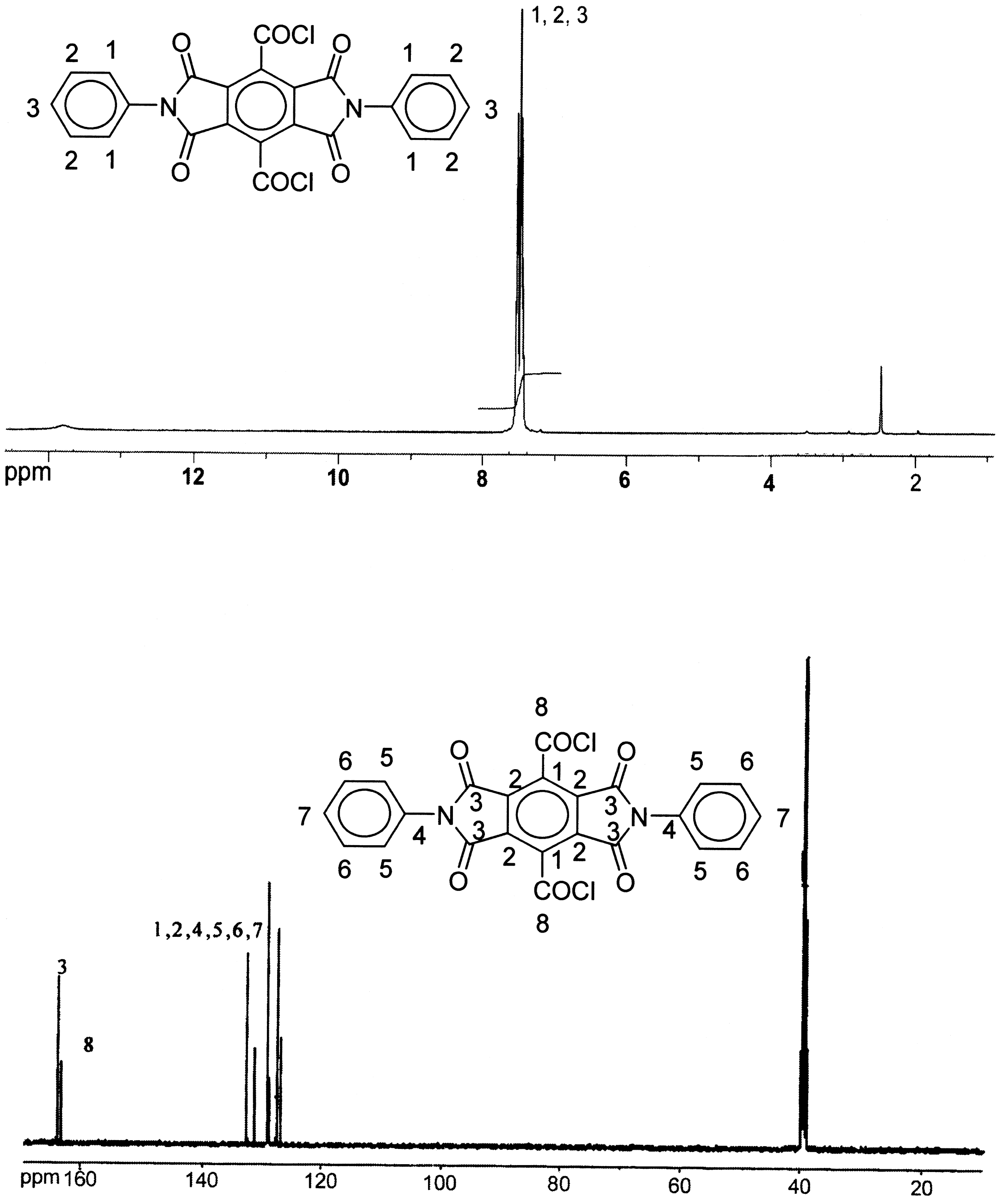


Figure 1. The ^{1}H and ^{13}C NMR Spectra of *N,N'*-diphenyl-2,3,5,6-diimido benzene-1,4-dicarboxylic acid chloride (PIBAC).

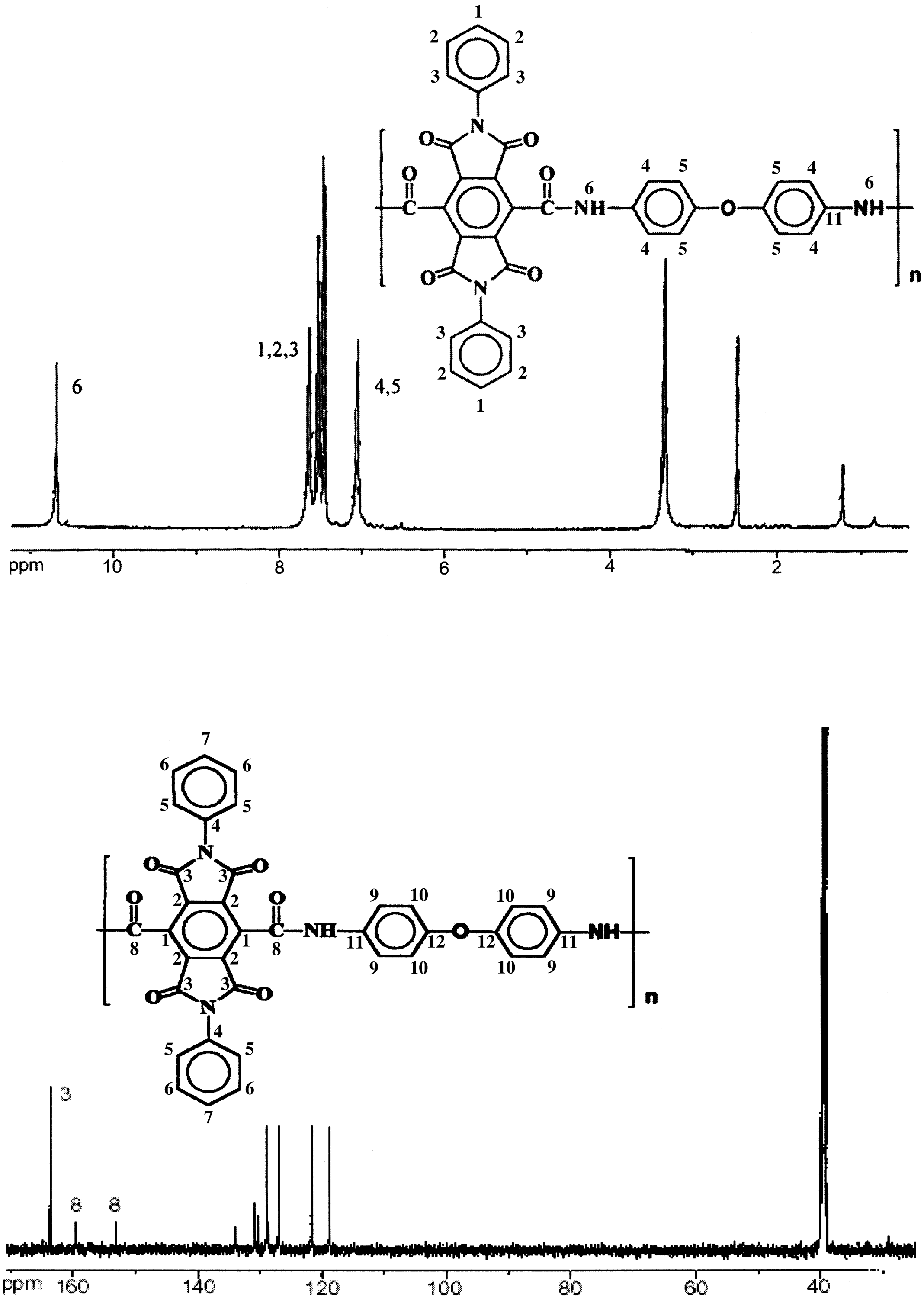


Figure 2. The ^{1}H and ^{13}C NMR Spectra of III-a measured in DMSO-d_6 at room temperature.

Various polyamides were prepared by a polycondensation reaction of PIBAC with the corresponding aromatic diamines (Scheme 1). In this reaction, a reaction system was exothermic. In the first stage, it was needed to remove the heat of reaction so as to prevent the other side reaction. After a few minutes, there was no more exothermic reaction. In the second stage, the polymerization reaction performed at 80°C for 2 hours, and we used a catalytic amount of pyridine as a organic base to capture hydrogen chloride (HCl) generated in this polycondensation. The results of the polycondensation are listed in Table 1. All polyamides were obtained with quantitative yield except for PIBAC/SDA. Inherent viscosities of each polyamide ranged from 0.35 to 0.8 dl/g. The unsatisfactory result obtained from sulfonedianiline was caused by poor solubility of the resulting polyamide and the low reactivity of the diamine. Especially, in the case of using *p*-phenylenediamine as a monomer, the reaction solution swelled at once as soon as the reaction started, so we could not obtain the high molecular weight polymer from PIBAC and *P*-PDA.

Polymer Properties

As shown in Figure 3, the respresentive a and b polyamides exhibited almost semi-crystalline pattern in every case due to a lower packing of the unsymmetrical polymer backbones.

FTIR spectra of the polymers showed a characteristic amide band of the –N-H stretching at 3200-3300 and 1650-1670 cm^{-1}. The ^1H-NMR spectrum of III-a is shown in Figure 2. The groups on the amide protons resonated at $\delta = 10.65$, whereas aromatic protons of main chain and the pendant imido phenyl unit resonated at $\delta = 6.5$-7.5. Integration ratios confirmed the expected structure and the absence of any signals arising from the possible end groups confirming the high polymeric nature of the product. The solubility of aromatic polyamides synthesized in this study was determined for the powdery samples in excess solvents and the results are listed in Table 2. All polymers were soluble in various aprotic polar solvents such as DMAc, DMF, and NMP. Their flexible pendant phenyl rings and low crystallinity may account for the good solubility of these polyamides.

Table 1. Characteristics of Polyamides by Direct Polycondensation Reaction of PIBAC and Some Diamines

	Yields (%)	$\eta_{inh}{}^{a}$ (dl/g)	T_d (°C)
III – a	98	0.83	400
III – b	99	0.68	398
III – c	96	0.35	320

[a] Measured at concentration of 0.5 g/dl in DMAc at 30 °C.

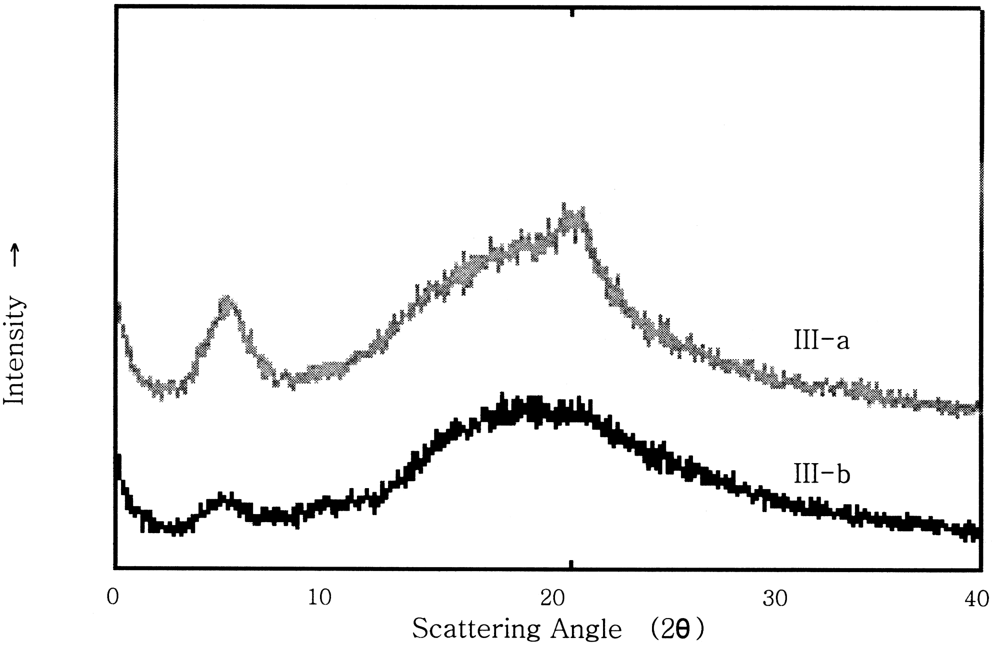


Figure 3. X-ray diffraction diagrams of polymers.

T_g was not detected in DSC experiments (Figure 4). The thermal resistance was investigated by TGA. Samples of polymers were subjected to a heating program under N_2 in order to elucidate how the chemical structure influenced the value of initial decomposition temperature, and the results are listed in Table 1. The nature of the diamine moiety greatly influenced the thermal resistance as was expected. The TGA curve represented in Figure 4 shows a weight loss step at first that must be attributed to the initial loss of side groups, and the second one shows the generation of homolytic degradation. Arnold has described the loss of pendant aromatic groups during the thermal analysis (TGA) of heat resistant polybenzotriazoles. In our case, PIBAC/SDA clearly shows a two-step decomposition, but such

Table 2. The Solubilities of Resulting Aromatic Polyamides Having Two Pendant *N*-Phenyl Imido Groups

	H_2SO_4	NMP	DMSO	DMF	THF	$CHCl_3$
III – a	+ −	+ +	+ +	+ +	+ −	− −
III – b	+ −	+ +	+ +	+ +	+ −	− −
III – c	+ −	+ +	+ +	+ +	+ −	− −

(+ +) Soluble, (+ −) Partially Soluble by heating, (− −) Insoluble.

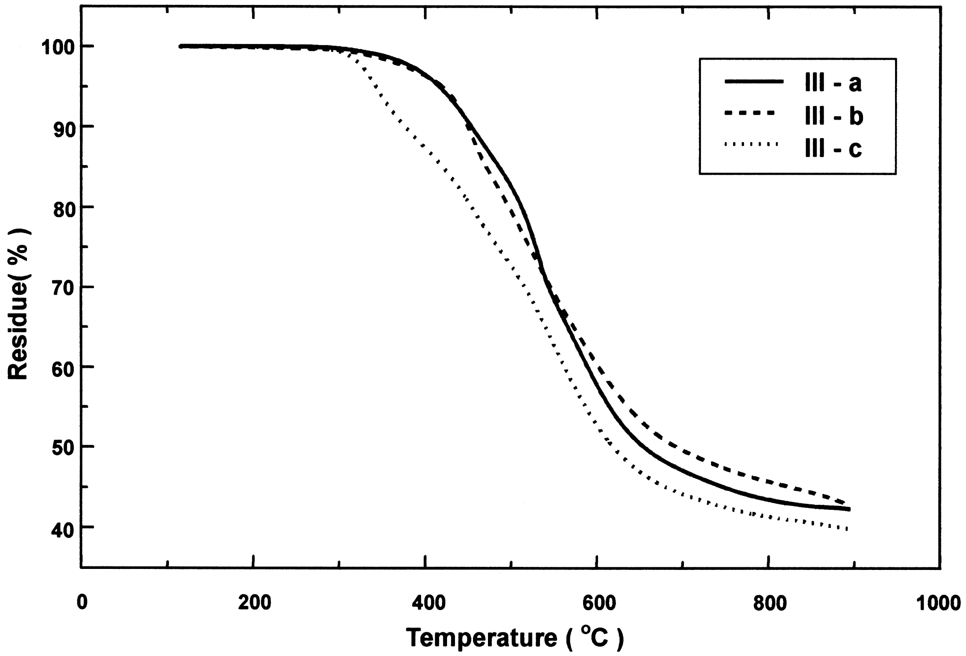


Figure 4. TGA thermograms of polyamides.

PIBAC/ODA and PIBAC/MDA do not show two-step decompositions, but single decompositions, so, we assumed that the pendant phenyl imido groups of PIBAC/ODA, PIBAC/MDA were more stable than that of PIBAC/SDA. Transparent, tough films of these polymers could be obtained from PIBAC/ODA, PIBAC/MDA by casting from their DMAc solutions due to its high inherent viscosity, but we could not obtain a tough film from PIBAC/SDA/DMAc solutions because its molecular weight was lower than others.

As shown in Figure 4, the resulting polyamides of the thermal decomposition are in the range of 320-400°C; they are quite thermally stable. A transparent flexible and tough film was cast.

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