Synthesis and the properties of novel cycloaliphatic-aromatic polyamides having pendent *N,N'*-diphenyl imido groups

Sang Hyun Park[1], Jae Wook Lee[1], Dong Hack Suh[2],*

[1] Department of Chemical Engineering, Sogang University, Seoul, Korea

[2] Department of Industrial Chemistry, Hanyang University, Seong dong-Gu, Seoul 133-791, Korea

ABSTRACT: We have investigated a novel monomer having two pendent phenyl imido groups for preparing new cycloaliphatic-aromatic polyamides. Novel polyamides were synthesized by direct polycondensation reaction of *N,N'*-diphenyl-2,3,5,6-diimido cyclohexane-1,4-dicarboxylic acid(PICA) and various aromatic diamines such as *p*-phenylene diamine, 4,4'-oxydianiline and 4,4'-methylene dianiline. A direct polycondensation was carried out by a Yamazaki method which is typical of using triphenyl phosphite, lithium chloride, and pyridine. Inherent viscosity of these resulting polyamides are ranged 0.20~0.45 dl/g. A transparent flexible and tough film was casted. The glass transition temperature of the polyamide from the PICA and 4,4'-oxydianiline is 147 °C. The decomposition temperature of these polyamides are ranged from 350 ~ 360 °C and the ash contents of them orders MDA > p-PDA > ODA according to kinds of the using diamines. And the solubilities of these polyamides are good in aprotic solvents such as DMAc, NMP, DMF.

INTRODUCTION

Aromatic polyamides have been widely used in industry because of their good thermal stability, good chemical resistance, and good mechanical properties. But they have some disadvantages like that most of aromatic polyamides cannot be dissolved in most organic solvents and be difficult to process due to intermolecular hydrogen bonding and their easy crystallization.[1] In order to improve solubility and maintain thermal stability, it has been performed that some studies of introducing soft segments to the main chain of the polymers, breaking its symmetry and regularity thereby making crystallization impossible, introducing bulky side groups to be exempt from the crystallization and breaking the hydrogen bonding by *N*-substitution of amide with certain groups.[2-12]

Up to 1960', aliphatic-aromatic polyamides from aliphatic diamines and aromatic diacid have been studied in great detail, but less is known about aromatic-aliphatic polyanides because of

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* Corresponding author

the difficulty of preparing them from aromatic diamines and aliphatic diacid by interfacial and solution method.[16, 17] Moreover, a little is known about the synthesis of polycondensation polymer starting from alicyclic diacids and aromatic diamines. The literature on alicyclic polyamides is fairly extensive, but has been focused mainly on the polyamides containing cyclic diamine and relatively less on the polyamides containing cyclic diacid. In the 1970s, Yamazaki and coworkers reported a direct polycondensation for the synthesis of polyamides. In this method, polyamides were synthesized by the direct polycondensation of aliphatic dicarboxylic acids with aromatic diamines in NMP containing metal salts. Triphenyl or diphenyl phosphite and pyridine were used as condensing agents. According to their investigation, this procedure could produce a high yield of polymers at a high molecular weight.

We expected that the introducing of alicyclic structure to the main chain of polymer could improve the solubility of the polymers and excellent thermal stability due to rigidity of the alicyclic structure.[14] The chair form of the cyclohexane ring could contribute to the rigidity in the polymer backbone.[15] Moreover, the polymers having alicyclic structures in a main chain are transparency and colorless because the charges in the aromatic structure of the polymers cannot transfer to the neighboring structure along the polymer main chain and are semicrystalline, most of which have amorphous.

We synthesized a new monomer, an alicyclic diacid of *N,N'*-diphenyl-2,3,5,6-diimido cyclohexane-1,4-dicarboxylic acid(PICA) using by ozonolysis reaction and oxidative work-up and polymerized a new class of polyamides of PICA and the diamines by Yamazaki polycondensation reaction.

EXPERIMENTAL PART

Materials

All chemicals were purchased from Aldrich, Junsei and Merck chemical company. 1,4-phenylenediamine(p-PDA), 4,4'-oxydianiline(ODA), 4,4'-methylene dianiline(MDA) were purified by a vacuum sublimation method. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150 °C for 6 hr and 180 °C for 10 hr. *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. And pyridine was refluxed with KOH overnight, distilled at atmospheric pressure and stored over molecular sieves 4 Å.

Characterization and Equipments

For the ozonolysis, ozone was generated by electronic discharge in an oxygen stream, using a Fisher 500 ozone generator. Ozone concentration in oxygen, which served also as a carrier gas, averaged 4 ~ 5 g/l. The ozone concentration was determined by percolation of an ozone-oxygen mixture through a 2% aqueous solution of potassium iodide(KI) and subsequent titration of the liberated iodine with a 0.1N aqueous sodiumthiosulfate($Na_2S_2O_3$) solution. ^{1}H-NMR and ^{13}C-NMR spectra were obtained by a Bruker 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 taken 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 was performed with a TA instruments Dupont Model 951 at a heating rate of 10 °C/min under nitrogen. Mass spectra recorded on a Jeol JMS-DX 303 GC/MS system using an electron impact method. Gel permeation chlomatography was carried out with Water Model 150C using μ -stagel columns

with DMF as an eluent solvent. The crystallinity of the polymers was examined by X-ray diffraction diagrams using the powder method with the use of nickel-filtered Cu K_α radiation. The viscosities were measured in a 0.4mm(i.d.) Ostwald viscometer at 30.0 ±0.1 °C with 0.5g/dL of polymer concentration in DMAc.

Synthesis of *N,N'*-diphenyl-2,3,5,6-diimido bicyclo[2.2.2]oct-7-ene(PICO)

A 500ml, two-neck, round-bottomed flask was equipped with a stirrer and was charged with 500ml anhydrous DMAc, 24.4g (0.1mol) of Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and 18.4ml (0.202mol) of distilled aniline. The solution was heated up to 100 °C and kept for 4 hr. After that procedure, 25 ml of toluene was added into the solution and then the Dean-Stark trap equipped with containing 25ml toluene. An azeotropic mixture of water and toluene was removed by the imidization reaction for 5 hrs. : Yield 95%, mp 317°C; ^{1}H NMR(DMSO-d_6) δ 3.41(4H, H-2,3,5,6), 3.54(2H, d, $J_{1,7} = J_{4,8}$= 2.4, H-1,4), 6.31(2H, d, $J_{7,1} = J_{8,4}$ = 2.4, H-7,8), 7.16(4H, d, $J_{3',2'}$=7.3, H-2'), 7.40(2H, d, $J_{4',3}$=6.8, H-4'), 7.46(4H, DD, $J_{3',2'}$, $J_{3',4'}$=6.8, H3'); 13C NMR (DMSO-d_6) δ 33.92 (C-3'), 130.92 (C-2,3,5,6), 126.75 (C-2'), 128.36 (C-4'), 130.92 (C-78), 132.02 (C-1'); IR (KBr) 3050, 2950, 1770, 1702, 1590, 1490, 1380, 1300, 1187, 799, 745, 691 cm^{-1}.
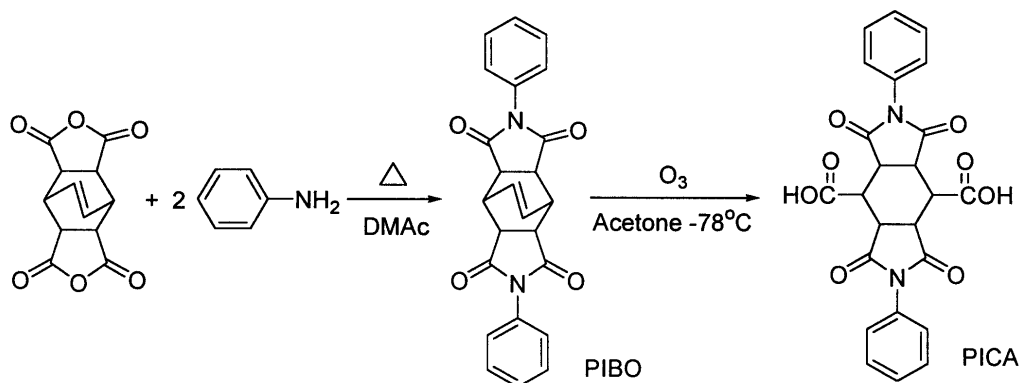
Scheme 1. Synthesis of *N, N'*-diphenyl-2,3,5,6-diimido cyclohexane-1,4-dicarboxylic acid(PICA)
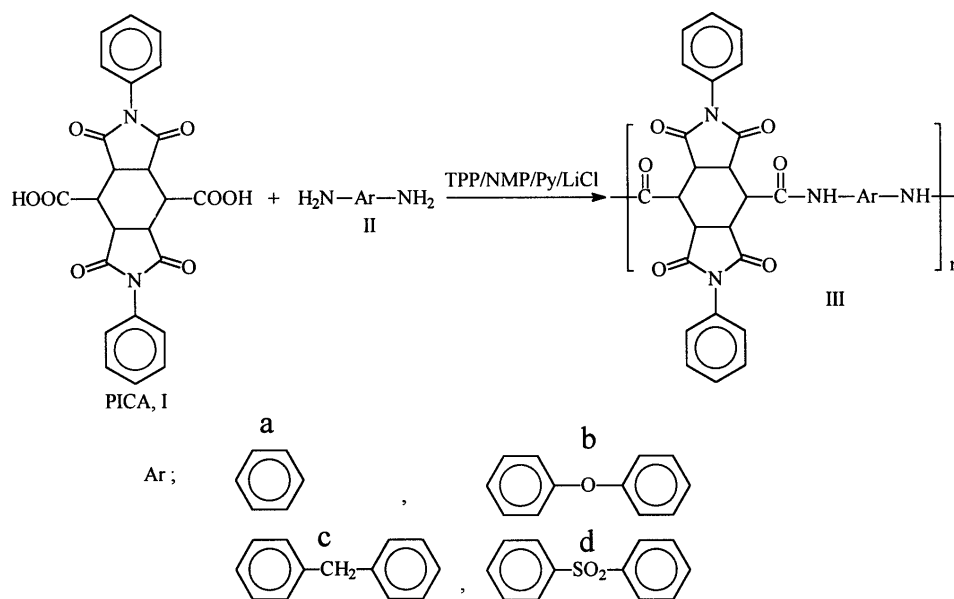
Synthesis of *N,N'*-diphenyl-2,3,5,6-diimido cyclohexane-1,4,-dicarboxylic acid(PICA)

10g (25mmol) of *N,N*-diphenylbicyclo[2.2.2]octene-2,3,4,5-tetracarboxylic diimide was dissolved in 1 L of acetone and transferred into the reactor. The solution was stirred and cooled to -78 °C and then the reaction was performed by continuous introduction of ozone. During the hole course of run, the gas stream was adjusted to the flow rate of 10 L/min through the reactor and contained at 0.5mole of ozone per liter of an O_3/O_2 mixed gas. The completion of the reaction was confirmed by the charge of color in KI trap (change to light-brown due to the excess ozone and iodine) and the O_3/O_2 mixed gas was stopped and then nitrogen was purged for ca. 20 minute to kick out the remained ozone in the reactor. Acetone was removed from the mixture by a rotary vacuum evaporator. The resulting product was dissolved in 200 ml of 90% formic acid and 100 ml of 30% hydrogen peroxide and carefully warmed to 60°C using a water bath. After the vigorous reaction was ceased, the mixture was again heated at 75°C for 6 hr. After the mixture was cool, excess formic acid was removed to give 7g of the resulting diacid. mp 222 °C (measured by DSC) dec;Ozonide I ^{13}NMR(DMSO-d_6): δ 25, 39, 48; Ozonide II δ 102, 120, 127.5, 129, 133, 176, 201.5, IR(KBr pellet) : 3471, 2940~2990, 1780, 1720, 692, 1500cm^{-1}; Anal. Calcd. for $C_{27}H_{24}O_8N_2$: C, 64.3; H, 4.8; N, 5.6; O, 25.4. Found: C, 62.9; H, 4.7;N, 5.2; O, 25.1.; PICA-A ^{1}H

NMR(DMSO-d_6): δ 3.5~4.1, 6.7~6.5, 12.7; ^{13}NMR(DMSO-d_6):δ 38.5, 49.5, 126.5~ 132.5, 171, 175; IR(KBr pellet) 3175, 2890, 1780, 1710, 691, 1500cm^{-1}; Anal Calcd for $C_{24}H_{18}O_8N_2$: C, 62.3; H, 3.9; N, 6.1; O, 27.7. Found: C, 62.2; H, 3.9;N, 6.0; O, 27.2.

Polymerization

A mixture of 0.462g(1mmol) PICA, 0.2g(1mmol) ODA, 0.14g LiCl, 0.621g(2mmol) triphenyl phosphite, 1ml of pyridine, and 2ml of NMP was stirred heated at 105°C for 3 hr. The solution was trickled into 100 ml of methanol, and then the white precipitate was obtained. And the polyamides was purified in the boiling methanol solution for 6 hr. The yield was quantitative. The inherent viscosity of polymer was 0.41 dl/g, measured at 0.5g/dl of concentration in DMAc at 30 °C.

Scheme 2. Synthesis of Polyamides

Results

Monomer Synthesis

N,N'-diphenyl-2,3,5,6-diimido bicyclo[2.2.2]octene(PICO) was obtained easily from Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and aniline by equimolar imidization reaction in DMAc. *N,N'*-diphenyl-2,3,5,6-diimido cyclohexane-1,4-dicarboxylic acid(PICA) was synthesized by ozonolysis reaction through which, we make ozoindes and followed by further oxidation of these ozonides[17,18] which, shown in Scheme 1. Hydrogen peroxide was used as the further oxidation reagent in formic acid solution. We had tried some cleavage oxidation reactions of PICO using reagent or catalyst such as Potassium permanganate, Periodate, ruthenium chloride and ozone. We did not have a good result to produce PICA in most of case using those reagent and catalysts but have only a good result in the case of ozonolysis and further oxidation. FTIR spectra of the PICA showed characteristic imide band at 1765~1775 and 1710~1720 cm^{-1}. The ^{1}H-NMR spectrum of the PICA taken in given Figure 1. Hydroxy protons on the carboxylic acid resonated at δ =12.5 whereas cycloaliphatic protons resonated at δ =3.0~4.5 and phenyl groups on the imide protons resonated at δ =6.5~7.5. Integration ratios confirmed the expected structure. On the basis of the shielding effect of carbon, the position of chemical shifts for carbon was readily assigned from 90° DEPT experiment in Figure 2.
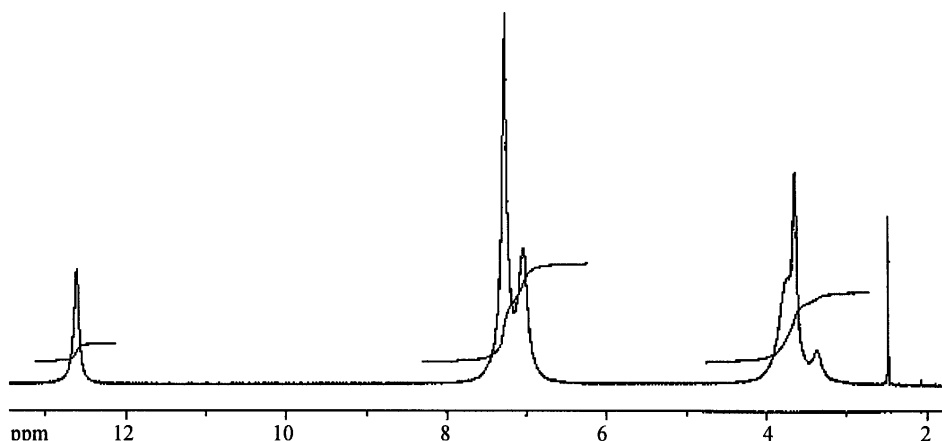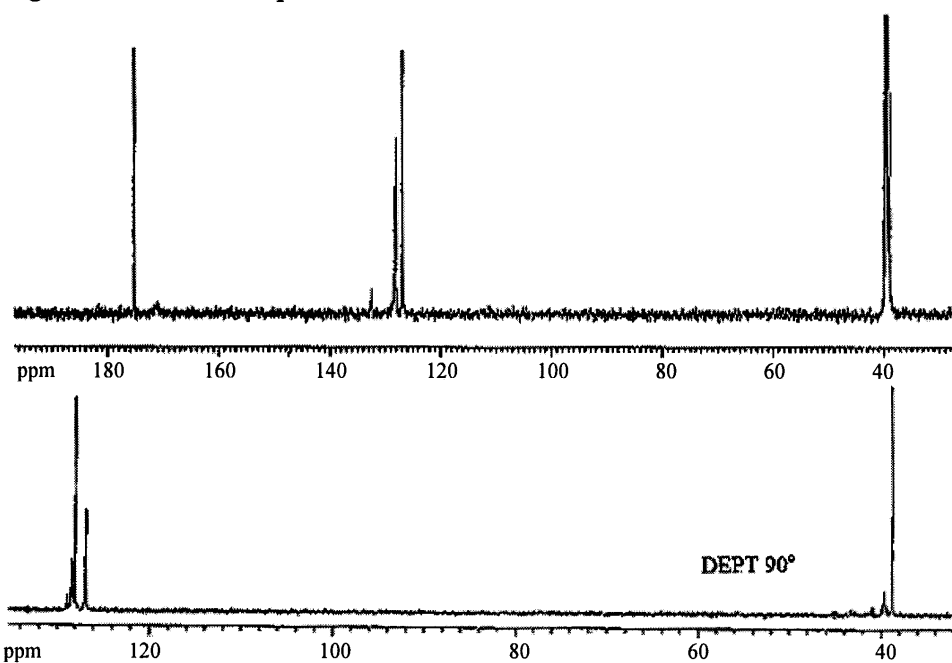
Fig 1. The ^{1}H-NMR spectrum of the PICA

Fig 2. The ^{13}C-NMR spectrum of the PICA

Synthesis of Polymers

Various polyamides were prepared from PICA with corresponding aromatic diamines by using the most favorable conditions. As shown in Scheme 2, polycondensation results are listed in table 1. All polyamides were obtained with a quantitative yield. Inherent viscosities of each polyamides are ranged from 0.2~0.45 dl/g. FTIR specra of the polymers showed characteristic amide band at 3200~3300 and 1650~1670 cm^{-1}. The ^{1}H-NMR spectrum of polymer III-a taken in given Figure 3. Phenyl groups on the amide protons resonated at δ =10.65 whereas the pendent imido phenyl unit resonated at δ =6.5~7.5 and cycloaliphatic protons of main chain resonated at δ =3.0~4.5. Integration ratios confirmed the expected structure and the absence of any signals arising from the possible end groups confirmed the high polymeric nature of the product. The elemental composition of the polymers is given in Table 1. In most cases, good agreement with the calculated values was obtained. Slight deviations were observed with some polymers, and these are attributed to molecularly bound NMP, which are extremely difficult to remove even under extensive vacuum treatment of the polymers at 100~150°C. The unsatisfactory results was obtained from *p*-phenylenediamine and sulfonedianiline caused by poor solubility of resulting polyamide and low reactivity of the

diamine, respectively. In the case of using *p*-PDA as the monomer, low molecular weight polymer was generated at the initial of polymerization.

Table.1 Characteristics of Polyamides by Direct Polycondensation Reaction of PICA and some Diamines

	Yields(%)	η_{inh}[a]	Tg/Td	Elementary Analysis		
PICA/*p*-PDA (III-a)	98	0.41	- / 385	Calcd	67.42	4.12	10.48
				Found	67.56	4.58	10.36
PICA/*m*-PDA(III-b)	95	0.24	132.3 / 378	Calcd	67.42	4.12	10.48
				Found	67.67	4.46	10.38
PICA/ODA (III-c)	99	0.45	147.8 / 369	Calcd	69.01	4.61	8.95
				Found	68.68	4.15	9.10
PICA/MDA (III-d)	96	0.35	137.8 / 376	Calcd	71.10	4.40	8.90
				Found	70.43	4.87	8.99

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

p-PDA : *p*-Phenylene diamine, *m*-PDA : *m*-Phenylene diamine, ODA : 4,4´ -Oxydianiline, MDA : 4,4´ - Methylene dianiline.

N. Yamazaki and F. Higashi investigated about optimum condition of polycondensation reaction of aromatic diacids with the diamines.[20] They suggested that the optimum reaction condition has LiCl concentration of 4 wt%, pyridine content in the mixture with NMP of 40 vol.%, temperature of 100°C, monomer concentration=0.6mol/l, molar ratio of monmer/triphenyl phosphite = 1:1, reaction duration=3hr. A Yamazaki reaction[21] made possible the direct synthesis of polyamide from aromatic diamines and various aliphatic diacids. Aromatic-aliphatic polyamides from 4,4'-oxydianiline and aliphatic diacids, those length of CH_2 are from 2~10. The glass transition temperatures of these polymers are in the range of 120~180°C.[22] But, the solubility of these polymers are poor or insoluble in most organic aprotic solvents. And F. Higashi suggested some advanced polycondensation method using $CaCl_2$ with LiCl as salts, using thionyl chloride as condensing agent in NMP.[23,24] We tried in order to increase the solubility and the above mentioned, but had better result in the case of Yamazaki polycondensation reaction using triphenyl phosphite, LiCl as a condensing agent in the solvents of pyridine and NMP.

Polymer Properties

X-ray diffraction confirmed that the polymers were semi-crystalline because of small portion of crystalline peaks in the X-ray diffraction diagrams as shown in Figure 3. Amorphous pattern in every case despite having small crystalline regions is due to lower packing of the unsymmetrical polymer backbones.
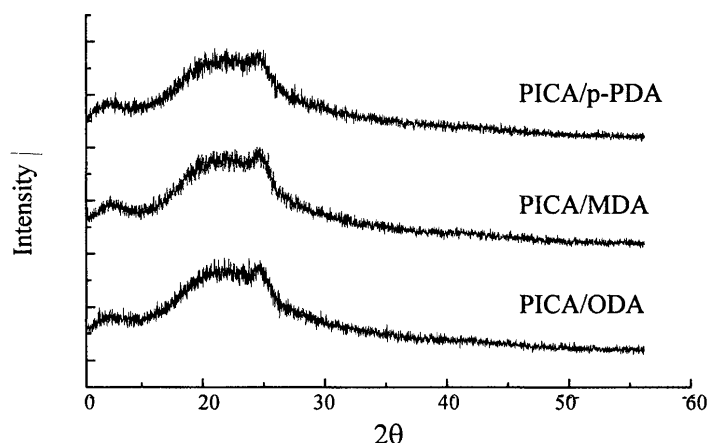

Fig 3. X-ray Diffraction Diagrams of Polyamides

The solubility of these cycloaliphatic-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 solvents such as DMAc, DMF, NMP, m-cresol and even THF and pyridine. The good solubility of these polyamides may be elucidated by their flexible pendent phenyl rings and low crystallinity.

Table.2 The Solubilities of Resulting Polyamides having Two Pendent *N*-Phenyl Imido Groups.

	H_2SO_4	NMP	DMSO	DMF	THF	$CHCl_3$
p-PDA (III-a)	+ −	+ +	+ +	+ +	− −	− −
m-PDA (III-b)	+ −	+ +	+ +	+ +	+ −	− −
ODA (III-c)	+ +	+ +	+ +	+ +	+ −	− −
MDA (III-d)	+ +	+ +	+ +	+ +	+ −	− −

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

p-PDA : *p*-Phenylene diamine, *m*-PDA : *m*-Phenylene diamine, ODA : 4,4´ -Oxydianiline, MDA : 4,4´ -Methylene dianiline.

Since the influence of residual water or solvent and history of thermal annealing are sometimes observed in the first heating run of DSC, the first heating of the samples was curtailed at 300°C; in addition, the T_g and other other thermal properties were evaluated according to the DSC charts of the second heating. There is evidence of glass transition temperatures of polymers whose results of thermograms are shown in Table 1.

Other polymers such as Polymer III-a, b, c exhibited a featureless trace up to a temperature of around 350°C, followed by the endothermic peak appearing at around 400°C, interpreted as a melting process accompanied by decomposition. Whose thermograms are shown Figure 4. No crystallization exotherms or melting endotherms were observed in any case up to temperature of 400°C, which was the temperature at which the polymers began to decompose. 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. The results have been listed in Table. The nature of the diamine moiety quite great influenced the thermal resistance as was expected. The TGA curve represented in Figure 4 shows at first weight loss step that must be attributed to the initial loss of side groups. Arnold has described to the loss of pendent aromatic groups during the thermal
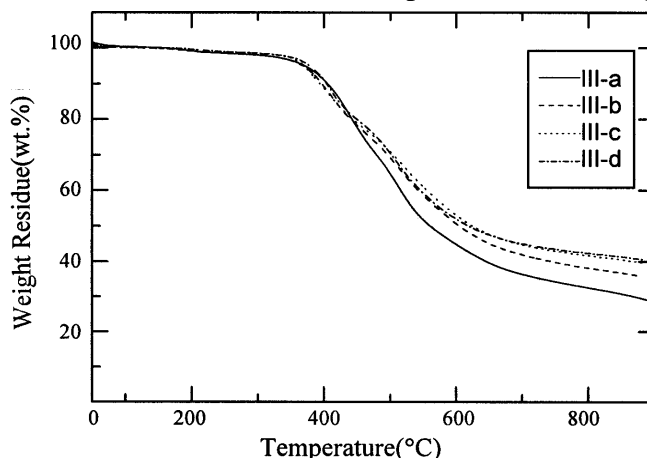

Fig 4. TGA Thermogram of Polyamides

analysis (TGA) of heat resistant polybenzotriazoles.[25] Transparent, brittle films of these polymers could obtained by casting from their DMAc solutions due to its low inherent viscosity.

Acknowledgement

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