

## Synthesis and Modifications of Nylons Having Bromine and Azide Functionality

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In this study, new aliphatic polyamides which containing bromine were synthesized by using 2,3-dibromosuccinyl chlorides and different long chain diamines. Polymerization was performed *via* interfacial polymerization. The polymers were characterized by FTIR, <sup>1</sup>H NMR, TG and viscosity measurement. According to the thermo-analytical, the thermal degradations of polyamides were increased by introduction of bromine moieties into polymer backbone. These aliphatic polyamides have inherent viscosities in the range of 0.19-0.65 dL/g in H<sub>2</sub>SO<sub>4</sub> at 25 °C. Solubility of these polymers also discussed. It is observed that polyamides with bromine increased flame-retardation and also these polymers may find use in a variety of click chemistry strategy because of azide functionality.

**Key Words:** Nylons, Aliphatic polyamide, Thermal degradation, Fibers, Thermostable polymers.

### INTRODUCTION

Polyamides are well recognized as a class of commercially important thermostable polymers. The ordering and varying of backbone functions have profound effects on the final properties such as solubility and thermal characteristics of polymers<sup>1-3</sup>. The investigation of thermally stable linear polyamide systems has received great emphasis because nylons are used in many demanding applications (such as laminates, films and fibers) where the properties of thermal stability and fire resistance are priorities<sup>4,5</sup>. Because of this high practical interest, the thermal decomposition of aliphatic nylons has been studied extensively.

The introduction of halogen units into the polymer backbone or side-chain has been explored as a convenient way to obtain thermally stable materials<sup>6-8</sup>. In this connection, it is thought that polyamides containing halogen units in the side chain possess can show good thermal stabilities<sup>9-13</sup>. So, to prepare polyamides with enhanced thermal stabilities, new monomers containing halogen groups can be introduced and used for preparation of polyamides. The incorporation of halogen units can provide beneficial effects for thermal stability and azide chemistry strategy for example; The "click"-type reactions, mainly hold up as by Huisgen 1,3-dipolar azide-alkyne, [3 + 2] or have attracted much attention due to their important features including high yields, high tolerance of functional groups and selectivity<sup>14-17</sup>. Huisgen 1,3-dipolar cycloaddition occurs between an alkyne and an organic azide to give triazole ring<sup>18-22</sup>. The reactions can be performed under

mild experimental conditions when catalyzed by copper(I). The development and the application of click chemistry in polymer and material science have recently been studied extensively<sup>23-28</sup>. Because of this approach, we have synthesized new nylons having side-chain bromine moieties and click functionality.

### EXPERIMENTAL

All chemicals and solvents used in this study were analytical grade. Main chemicals used in this study were as follow: 2,3-dibromosuccinic acid (98 %, Aldrich), phosphorous pentachloride (Merck), 1,4-diamino butane (98 %, Merck), 1,5-diaminopentane (98 %, Acros Organics), 1,6-diamino hexane (98 %, Merck), 1,7-diamino heptane (98 %, Alfa Aesar), 1,8-diamino octane (98 %, Aldrich), 1,9-diamino nonane (98 %, Alfa Aesar), dichloro methane (99 %, Riedel-de Haen), sodium hydroxide (Sigma) dimethyl sulphoxide (99 %, Riedel-de Haen), sodium azide (Sigma), sulphuric acid (98 %, Merck), trifluoroacetic acid (TFA) (99 % merck), trichloroacetic acid (90 % merck), formic acid (90 % merck).

Characterization of the polyamides was performed with a Perkin-Elmer Spectrum 100 FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded with a Varian 400 MHz NMR spectrometer in trifluoroacetic acid and DMSO as solvents at room temperature. The thermal analysis was performed in both N<sub>2</sub> and air (flow rate 100 mL/min) with a heating rate of 20 °C/min using a Perkin Elmer TG. All of the products were dried in vacuum oven at 25 °C on 10 mbar pressure before the thermal analyses. Viscosity determinations on the polymer

solutions are reported here as inherent viscosities determined at 25 °C in sulphuric acid with  $C = 0.5$  g/dL of solution using Ubbelohde viscometer.

**Synthesis of 2,3-dibromosuccinyl chlorides (BSC):** 5 mmol 2,3-dibromosuccinic acid was treated with two equivalents of phosphorous pentachloride. The mixture melted at 50 °C and turned the red liquid. Then solution was stirred at 100 °C for 5 h. The resulting solution was allowed to stir at 25 °C overnight. Liquid was decanted from small amount of residue and separated from phosphorus oxychloride by distillation in a vacuum.  $^1\text{H}$  NMR ( $\text{CDCl}_3-d_6$ ):  $\delta$  5.0 (d 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3-d_6$ ):  $\delta$  48.8 and 164.2. FTIR  $\nu$ , T ( $\text{cm}^{-1}$ ): 2968-2910 ( $-\text{CH}_2$ ), 1780 ( $\text{C}=\text{O}$ ).

**Synthesis of poly(hexamethylene dibromosuccinamide) (PAB64):** The synthesis of PAB64 by interfacial polycondensation was accomplished with 5 mmol of 2,3-dibromosuccinyl chlorides in 25 mL of dichloromethane (solution 1). Over this solution was added solution 2, containing 5 mmol of hexamethylenediamine and 10 mmol sodium hydroxide in 25 mL distilled water. The polymerization reaction started immediately as soon as the addition of solution 2. All other polymers and copolymers (Table-1) were synthesized above procedure.  $^1\text{H}$  NMR ( $\text{TFA}-d_6$ ):  $\delta$  1.5-1.7 (b 4H), 1.7-2.0 (b 4H), 3.8 (m 8H), 5.1 (d 2H). FTIR  $\nu$ , T ( $\text{cm}^{-1}$ ): 3304  $\text{cm}^{-1}$  (N-H), 2968-2910 ( $-\text{CH}_2$ ), 1639 ( $\text{C}=\text{O}$ ), 1540 (amide II).

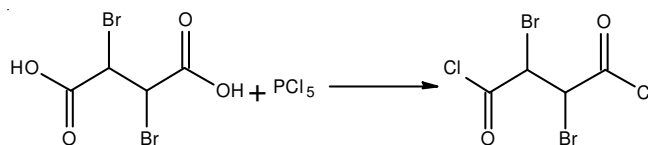
TABLE-1  
SAMPLES USED FOR POLYAMIDES  
INTERFACIAL POLYMERIZATION

Samples	Polyamides
PAB44	$\left[ \text{NH}-(\text{CH}_2)_4-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PAB54	$\left[ \text{NH}-(\text{CH}_2)_5-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PAB64	$\left[ \text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PAB74	$\left[ \text{NH}-(\text{CH}_2)_7-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PA74	$\left[ \text{NH}-(\text{CH}_2)_7-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_2-\text{C}(=\text{O}) \right]_n$
PAB84	$\left[ \text{NH}-(\text{CH}_2)_8-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PAB94	$\left[ \text{NH}-(\text{CH}_2)_9-\text{NH}-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}(\text{Br})-\text{C}(=\text{O}) \right]_n$
PA66	$\left[ \text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O}) \right]_n$

**Synthesis of azide functional polyamide (PA64-N3):** PA64 (1.0 g) was dissolved in dimethyl sulfoxide (20 mL),  $\text{NaN}_3$  (0.36 g) was added. The resulting solution was allowed to stir at 25 °C overnight and precipitated into methanol/water mixture (1/1 by volume). FTIR  $\nu$ , T ( $\text{cm}^{-1}$ ): 3392 (N-H), 2115 ( $-\text{N}_3$ ) 2968-2910 ( $-\text{CH}_2$ ), 1625 ( $\text{C}=\text{O}$ ), 1544 (amide II).

## RESULTS AND DISCUSSION

In present study, we first synthesized 2,3-dibromosuccinyl chlorides (Scheme-I). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of the 2,3-dibromosuccinyl chlorides are shown in Figs. 1 and 2, respectively. From the  $^1\text{H}$  NMR spectrum of 2,3-dibromosuccinyl chlorides, the (Br-CH-CH-Br) protons peak were detected 5 ppm. In the  $^{13}\text{C}$  NMR spectrum of 2,3-dibromosuccinyl chlorides, the peaks at 48.8 and 164.2 ppm are assigned to Br-CH-CH-Br and Cl-CO- carbons, respectively.



Scheme-I: Synthesis of 2,3-dibromosuccinyl chlorides

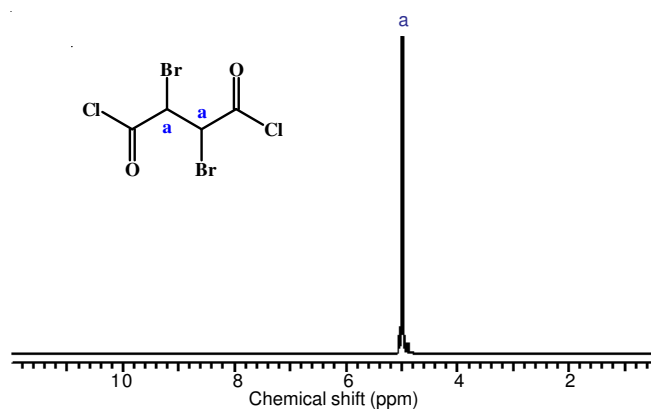


Fig. 1.  $^1\text{H}$  NMR spectra of 2,3-dibromosuccinyl chlorides

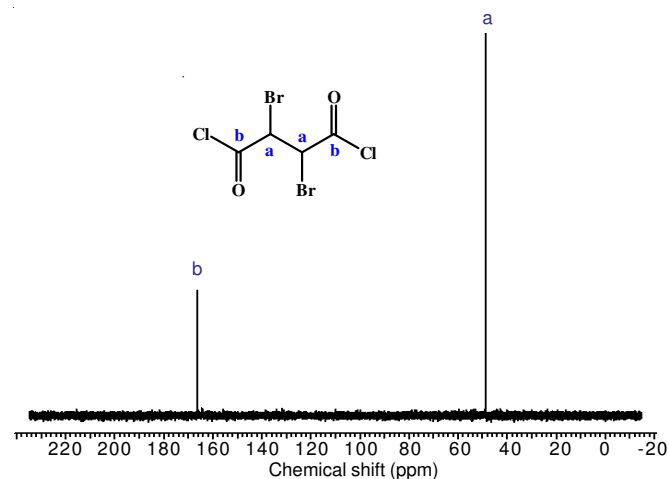
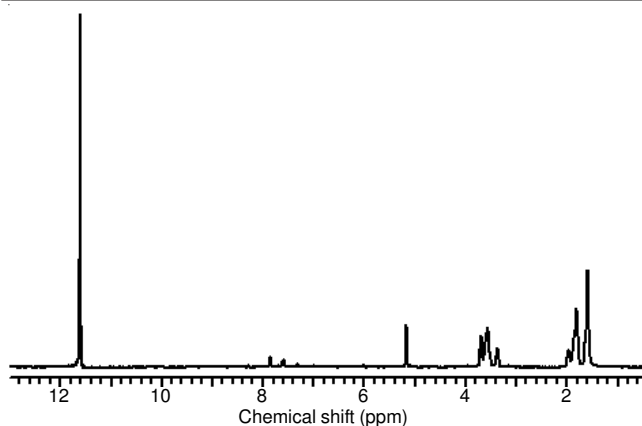


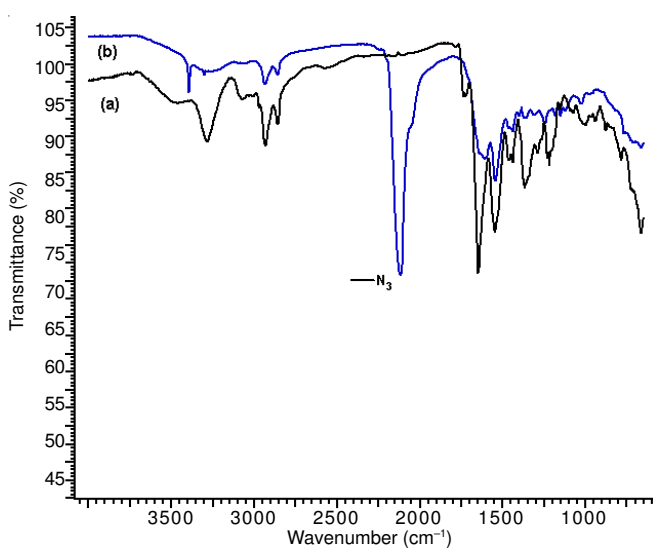
Fig. 2.  $^{13}\text{C}$  NMR spectra of 2,3-dibromosuccinyl chlorides

All polyamides confirmed by  $^1\text{H}$  NMR and FTIR. From the  $^1\text{H}$  NMR spectrum of the PAB64 (Fig. 3), the  $\text{NH}-(\text{CH}_2)_2-(\text{CH}_2)_2-(\text{CH}_2)_2-\text{NH}$  and  $\text{CO}-(\text{CH}_2)_2-\text{CO}$  protons were detectable as multiple peaks between 1.5-1.7 and 1.7-2.0 ppm. Additionally,  $\text{NH}-(\text{CH}_2)_2-$  protons are observed as multiple peaks between 3.08 and 3.68 ppm. The  $^1\text{H}$  NMR spectrum of PAB64 is also showed two unexpected new signals. One of them is a singlet 5.1 ppm and second one is between 7.5 and 7.8 ppm which are assigned to  $-\text{BrCH}-\text{CHBr}-$  and  $\text{CH}=\text{C}$ , respectively.

Fig. 3.  $^1\text{H}$  NMR spectra of PAB64

We estimated that this peaks (CH=C) occurred with elimination of bromine. This state has been reflected all stages of  $^1\text{H}$  NMR spectrums of all other polyamides.

The samples of polyamides were also characterized by Fourier-transform IR analysis. Fig. 4 shows the FTIR confirmed the chemical structure of the PAB64 showing absorptions for all required chemical groups: N-H stretch around at  $3300\text{ cm}^{-1}$ , C-H stretch around at  $2940\text{--}2860\text{ cm}^{-1}$ , amide-I around at  $1632\text{ cm}^{-1}$  and amide-II around at  $1540\text{ cm}^{-1}$ .

Fig. 4. FTIR spectra of (a) PAB64 and (b) PA64- $\text{N}_3$ 

The structure of PAB64- $\text{N}_3$  was supported by the observation of the azide stretching band at  $2115\text{ cm}^{-1}$  in the FTIR spectrum of PAB64- $\text{N}_3$  (Fig. 4). Comparing these results, it is observed that the spectra present several coincident peaks showing the success of this synthesis.

The yield and inherent viscosity results of polyamides were given at Table-2. The yields of synthesized polyamides and inherent viscosity values were increased with the number of carbon in the amine chain. Inherent viscosity values of polyamides between 0.16-0.65 dL/g which roughly correspond to molecular weight of 6000-45000 g/mol<sup>13</sup>. Polyamides with long chain diamine showed higher viscosity than other ones. In addition inherent viscosity was increased with the proportion PA66 in the polyamide copolymer (PA66-co-PAB64).

TABLE-2  
POLYMERIZATION YIELD AND VISCOSITY OF POLYMERS

Poyamides	Yield (%)	Inherent viscosity (dL/g)*
PAB44	23	0.16
PAB54	24	0.18
PAB64	29	0.25
PAB74	29	0.28
PA74	50	0.11
PAB84	34	0.33
PAB94	38	0.42
PA66	90	0.95
20 % PA66-co-PAB64	42	0.65

\*Measured at a concentration of 0.5 g/dL in  $\text{H}_2\text{SO}_4$  an  $25\text{ }^\circ\text{C}$ .

We used various solvent to test the solubility of the polyamides. Solubility of the polyamides was changed polarity in their structure. The results of solubility of polymers were given at Table-3.

TABLE-3  
SOLUBILITY OF POLYAMIDES IN VARIOUS SOLVENT

Polyamides	DMSO	TCA	FA	THF	DCM	DEE	CYHEX
PAB44	+	+	-	-	-	-	-
PAB54	+	+	-	-	-	-	-
PAB64	+	+	-	-	-	-	-
PAB74	+	+	-	-	-	-	-
PA74	-	+	+	-	-	-	-
PAB84	+	+	-	-	-	-	-
PAB94	+	+	-	-	-	-	-
20 % PA66-co-PAB64	+	+	+	-	-	-	-

+: Soluble, -: Insoluble; TCA = Trichloroacetic acid; FA = Formic acid, THF = Tetrahydrofuran; DCM = Dichloromethane; CYHEX = Cyclohexane.

Thermal properties of the 10 % weight loss ( $T_{10}$ ) of the polymers and residue at  $900\text{ }^\circ\text{C}$  (char yield) were used as criterions for their thermal stability. All polyamides were heated under both nitrogen and air. Results were shown at Table-4 and Figs. 5 and 6. According to the thermal analysis results in air, 10 % weight loss thermal degradations temperatures ( $T_{10\%}$ ) of polyamides were observed between  $226\text{--}284\text{ }^\circ\text{C}$ , but the thermal analysis performed under  $\text{N}_2$ ,  $T_{10\%}$  decomposition temperature was observed between  $242\text{--}282\text{ }^\circ\text{C}$ .

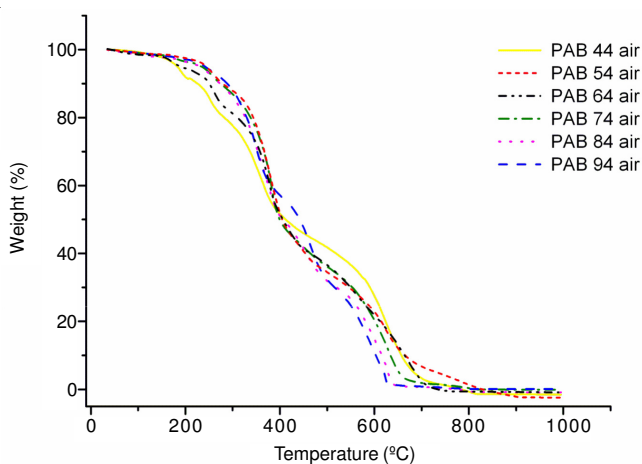


Fig. 5. Thermal degradation of polyamides in air

TABLE-4  
TGA ANALYSIS OF POLYAMIDES

Polymer	T <sub>10</sub> (°C)	Char yield (%) 900 °C
PAB44 in N <sub>2</sub>	242	27
PAB44 in Air	226	–
PAB54 in N <sub>2</sub>	247	25
PAB54 in Air	250	–
PAB64 in N <sub>2</sub>	257	26
PAB64 in Air	252	–
PAB74 in N <sub>2</sub>	272	21
PA74 in N <sub>2</sub>	205	5
PAB74 in Air	270	–
PAB84 in N <sub>2</sub>	282	18
PAB84 in Air	272	–
PAB94 in N <sub>2</sub>	282	14
PAB94 in Air	284	–
PA66 in N <sub>2</sub>	270	4
20 % PA66-co-PAB64 in N <sub>2</sub>	310	24

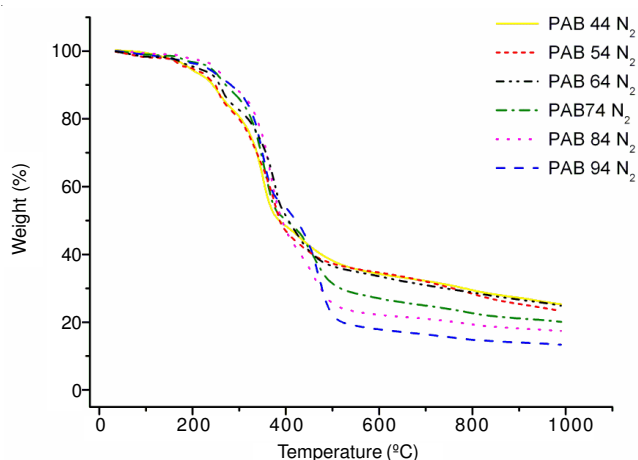


Fig. 6. Thermal degradation of polyamides in nitrogen

## Conclusion

In summary, we have demonstrated that polyamides with side-chain bromine moieties were described. Polyamides with bromine exhibited much more thermal stability than polyamides without substituent bromine. This is important for applications because of the increasing flame-retarded.

Moreover, we show click functionality of polyamides because it may find use in a variety of click chemistry strategy.

Polyamides have good resistance to solvents. However, good solvents for polyamides are strong acids such as H<sub>2</sub>SO<sub>4</sub>, trichloroacetic acid and formic acid.

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