

# Synthesis and Properties of Novel Aliphatic - Aromatic Polyamides Containing Benzofluoranthene Linkage

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## ABSTRACT

Novel aliphatic-aromatic polyamides are synthesized via polycondensation reactions of 7,12-dimethylcarboxylate benzo [k] fluoranthene with ethylenediamine, 1,3-propylenediamine and 1,6-hexamethylenediamine. Amidation of this diester is carried out by the melt technique. The resulted polyamides are characterized by spectroscopic methods. Some physical and thermal properties of these new polymers are studied and reported.

## Key Words

polyamides, benzo [k] fluoranthene, diamines, melt technique, polycondensation

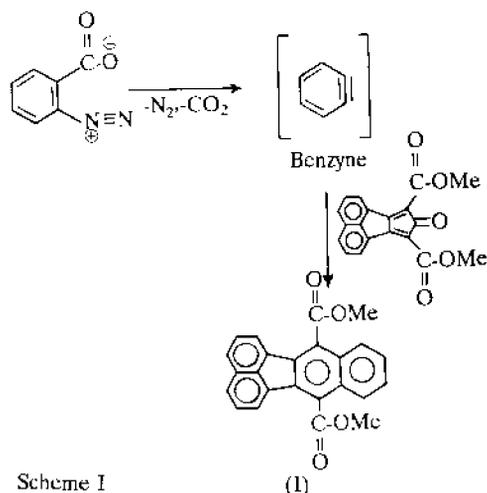
## INTRODUCTION

In general, the mechanical properties of aliphatic polyamides are impaired at temperatures above 150 °C. Properties are stabilized by incorporating aromatic or cycloaliphatic rings into the main polymer chain, which increases melting temperature  $T_m$ , glass-transition temperature  $T_g$ , and modulus. The properties depend on the flexibility of the aliphatic component, i.e. on the number of methylene groups in the main chain, and on the orientation of the connecting units (ortho, meta, or para). Aliphatic-aromatic polyamides have been synthesized and their properties and applications have been reported

[1-20].

In a previous paper [21], it was reported that benzyne, as a reactive intermediate, was trapped with 2-oxo-1,3-bis (methoxycarbonyl)-2-H-cyclopenta acenaphthylene via [4+2] Diels-Alder cycloaddition reaction. The resulted adduct 7, 12-dimethylcarboxylate benzo [k] fluoranthene (I) as a new monomer was obtained in quantitative yield (Scheme I).

The ready preparation of the diester monomer (I) prompted us to investigate its polycondensation reaction with different aliphatic diamines. Three different diamine monomers,



ethylenediamine, 1, 3-propylenediamine and 1, 6-hexamethylenediamine were selected for this investigation.

## EXPERIMENTAL

All melting points were taken with a Gallenham melting point apparatus and the values are uncorrected. Intrinsic viscosities were measured by the standard procedure using a Cannon-Fenske routine viscometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data for polymers were taken on a Stanton-650 DSC, TGA.

Proton nuclear magnetic resonance (H-NMR) spectra (90 MHz) were recorded on a Varian-EM-390 instrument.

Infrared (IR) spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies are reported in wavenumber ( $\text{cm}^{-1}$ ), with the intensity of the bands assigned the following classification: weak (w), medium (m), shoulder (sh), strong (s), broad (br).

Reagents were purchased from Fluka

Chemical Co., Aldrich Chemical Co. or Riedel-Dehaen AG. Ethylenediamine and propylenediamine were purified via vacuum distillation before use. 1, 6-Hexamethylenediamine was purified by sublimation.

### Synthesis Polyamide (II)

Into a stainless steel reactor which was equipped with a thick-wall glass tube and a gas release valve, was placed 2.0 g ( $5.4 \times 10^{-3}$  mol) of diester monomer (I), 5.0 ml ( $7.4 \times 10^{-2}$  mol) of ethylenediamine and 0.02 g of antimony trioxide. The valve was closed and the reactor was heated at 240 °C by a sand bath for 35 min. Then the side arm was connected to a vacuum pump (less than 1 mm/Hg) and heating was continued at 280 °C for 4 hours. The reactor was cooled and the product was dissolved in 35 ml of dimethylsulfoxide (DMSO) and it was precipitated in 450 ml of distilled water. The yellow solid was filtered, dried under vacuum at 110 °C for 6 hours to give 1.64 g (83%) of yellow solid, m.p. 300 °C (dec).

IR (KBr): 3365 (w), 3035 (m), 2920 (w,sh), 1703 (s), 1605 (w), 1483 (w), 1425 (m), 1347 (w), 1295 (w), 1235 (s), 1155 (w), 1095 (w), 885 (m), 820 (m), 770 (s), 475 (w,sh),  $\text{cm}^{-1}$ .

### Synthesis of Polyamide (II): Oligomer

Polymerization reaction was carried out in a similar way, but in the first stage the reactor was heated at 235 °C for 35 min., and in the second stage was heated at 245 °C under vacuum (about 10-12 mm Hg) for 15 min. The product was triturated with 35 ml of methanol, then washed with chloroform to remove unreacted monomers. The yellow solid was dried, m.p. 260 °C (dec).

IR (KBr): 3365 (w), 3035 (m), 2920 (w,sh), 1703 (s), 1605 (w), 1483 (w), 1425 (m), 1347 (w), 1295 (m), 1235 (s), 1155 (w), 1095 (w), 885 (m), 820 (m), 770 (s), 745 (w,sh)  $\text{cm}^{-1}$ .

### Synthesis of Polyamide (III)

2.0 g ( $5.4 \times 10^{-3}$  mol) of diester monomer (I), 5 ml ( $5.9 \times 10^{-2}$  mol) of propylenediamine and 0.02 g of antimony trioxide were placed into a stainless steel reactor and the procedure for the synthesis of

polyamide (II) was reported. The yellow solid, 1.47 g (86%), m.p. 285 °C (dec) was obtained.

IR (KBr): 3380 (m), 3035 (m), 2900 (w), 2540 (w), 1687 (s), 1575 (m), 1505 (w), 1485 (w), 1425 (s), 1360 (w), 1300 (m), 1235 (s), 1160 (m), 1040 (w), 1010 (w), 885 (w), 820 (m), 773 (s), 660 (w),  $\text{cm}^{-1}$ .

#### Synthesis of Polyamide (III): Oligomer

Polymerization reaction was performed in a similar manner to that described for the synthesis of the oligomer (II). The product was obtained as a yellow solid, m.p. 270 °C (dec).

IR (KBr): 3380 (m), 3035 (m), 2900 (w), 2540 (w), 1687 (s), 1575 (m), 1505 (w), 1485 (w), 1425 (s), 1360 (w), 1300 (m), 1235 (s), 1160 (m), 1040 (w), 1010 (w), 885 (w), 820 (m), 773 (s), 660 (w)  $\text{cm}^{-1}$ .

#### Synthesis of Polyamide (IV):

This polymer was prepared by the same procedure which was developed for the synthesis of polyamide II and III. The polymer was obtained as a pale-brown solid, 1.85 g (81%), m.p. 299 °C.(dec).

IR (KBr): 3390 (s), 3035 (s), 2920 (s), 1560 (s,br), 1405 (s), 1360 (m), 1320 (s), 1268 (m), 1165 (w), 1035 (w), 950 (w), 890 (w), 840 (w), 825 (w), 800 (w), 775 (m), 690 (m), 615 (w)  $\text{cm}^{-1}$ .

#### Synthesis of Polyamide (IV): Oligomer

Polymerization reaction was carried out in a similar manner to that described for the preparation of the oligomer II and III. The product was obtained as a yellow solid, m.p. 275 °C (dec).

IR (KBr): 3390 (s), 3035 (s,sh), 2920 (s), 1560 (s,br), 1405 (s), 1360 (w), 1320 (m), 1268 (m), 1165 (w), 1035 (w), 950 (w), 890 (w), 840 (w), 825 (w), 800 (w), 775 (m), 690 (m), 615 (w)  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

#### Preparation and Characterization of Polymers

Since monomer (I) is a diester, amidation reaction was used as a synthetic route for the polymerization reactions. Antimony trioxide was used as a catalyst in order to accelerate the

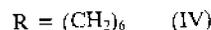
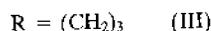
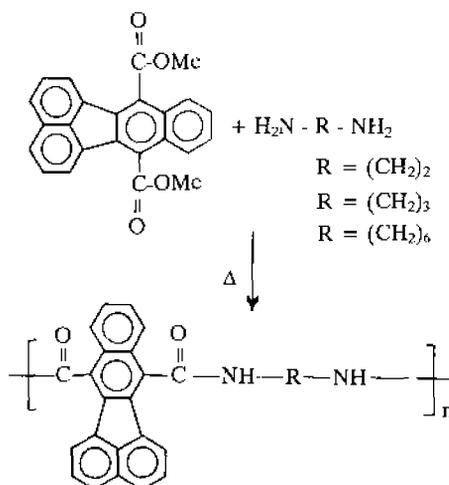
polycondensation reactions.

Polyamide (II) was prepared by the reaction of diester (I) with ethylenediamine (Scheme II). The reaction was performed in two stages. In the first stage diester (I) with ethylenediamine and catalyst were heated at 240 °C in a sealed reactor. In the second stage, the mixture was heated up to 280 °C under vacuum. The resulted polymer was obtained as a pale yellow solid.

The IR spectrum of polymer (II) showed two peaks for the N-H stretching and one peak for the carbonyl group (Table 1). These are characteristic patterns for the amide linkages.

Table 1. Infrared bond  $\text{cm}^{-1}$  (KBr) of polyamides.

Polymer	N-H stretching (free)	N-H stretching (hydrogen bonded)	C=O stretching
	II	3365	3035
III	3380	3035	1687
IV	3390	3035	1560



Scheme II

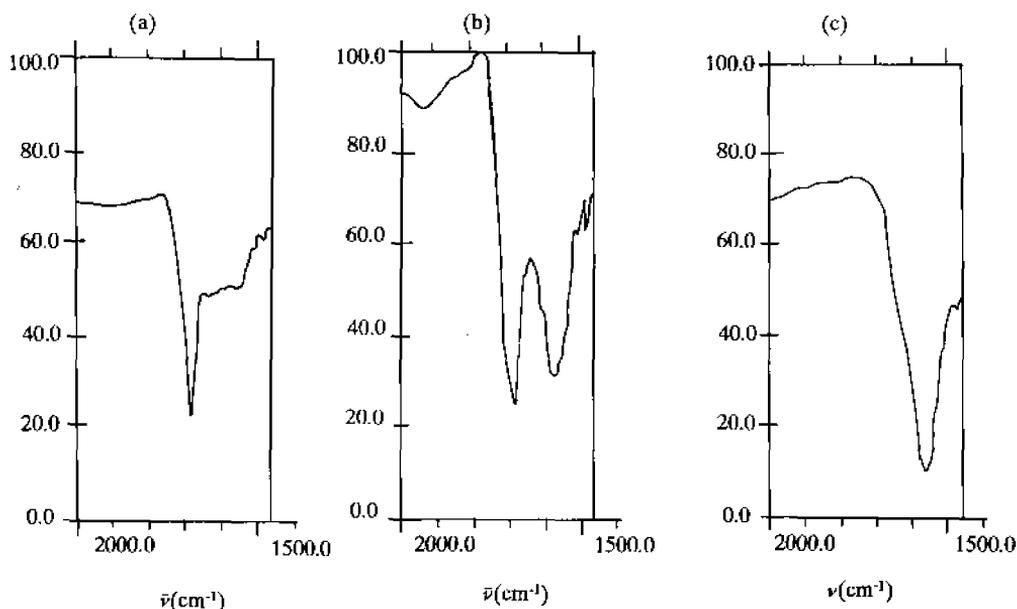


Fig.1. Infrared (KBr) spectra of polyamides (only carbonyl region): (a) polyamide (II), (b) polyamide (III), (c) polyamide (IV).

When monomer (I) was reacted with ethylenediamine at lower temperature and higher pressure, oligomer was obtained. The IR spectrum of this oligomer is similar to that of polyamide (II). Polyamide (III), oligomer (III), polyamide (IV) and oligomer (IV) were prepared in a similar manner. Their IR spectra (Table 1) are in agreement with the resulted polyamide structures.

A comparison of the IR spectra of polyamide (II), (III) and (IV) (only carbonyl region) gave very affirmative information about the extent of the intermolecular hydrogen bonding (Figure 1). In polyamide (II) with spacer group  $-(CH_2)_2-$  carbonyl group showed a strong peak at  $1703\text{ cm}^{-1}$ , which indicates that, the extent of the hydrogen bonding is very small. This can be attributed to the steric factor produced by the benzo [k] fluoranthene bulky group which prevents the strong  $C=O\dots H-N$

hydrogen bonding. In polymer (III) with spacer group  $-(CH_2)_3-$ , the carbonyl group shifts to the lower frequency ( $1687\text{ cm}^{-1}$ ), which indicates less steric hindrance, thus the extent of the hydrogen bonding increased. In polymer (IV) with spacer group  $-(CH_2)_6-$ , the carbonyl group showed peak at very low frequency ( $1560\text{ cm}^{-1}$ ), which also overlapped with  $C=C$  stretching, indicates that the extent of the hydrogen bonding is extremely high.

The H-NMR spectrum of oligomer (II) in  $D_2O$  showed a multiplet peak between 7.55-8.12 ppm which was assigned to the benzo [k] fluoranthene protons. The peaks at 2.65 ppm (triplet) were assigned to the methylene protons attached to the nitrogens atoms. The peak at 1.70 ppm (quintet) was assigned to the other methylene protons. The N-H peak was exchanged with  $D_2O$  and peak of water covered between 3-5 ppm. But,

when the H-NMR was recorded in DMSO, a broad peak at 5.55 ppm was observed for the N-H proton.

### Solubility and Thermal Properties

Solubility behavior of polyamide (II), (III), (IV) and their oligomers were determined for powdery samples in excess solvent. Oligomers (II), (III) and (IV) are not soluble in most organic solvents, but they are very soluble in water and showed very intense fluorescence. The chain length of low molecular weight oligomers are too short to permit entanglement. On the other hand, for steric reason the polymer chains cannot easily link together by hydrogen bonding and hence the small and polar molecules of water can penetrate into the oligomer molecules and make stronger hydrogen bonding with them and it causes the polymer to be soluble in water. However, the diester monomer (I) is not soluble in water at all.

Polymers (II), (III) and (IV) are not soluble in water. Polyamides (II) and (III) are soluble in some polar solvents like DMSO. But polyamide (IV) is soluble in concentrated sulfuric acid. Their intrinsic viscosities were measured in appropriate solvents and are summarized in Table 2.

Table 2. Intrinsic viscosities of polyamides.

Polymer	$[\mu]$ 25 °C dL/g	Solvent
II	0.08	DMSO
III	0.09	DMSO
IV	0.10	Conc.H <sub>2</sub> SO <sub>4</sub>

Softening points of the polyamides (II), (III) and (IV) were determined with a melting apparatus and DSC instrument and are summarized in Table 3. As the number of methylene spacer group increases the softening point decreases, but in the case of the polymer (IV), softening point increased. This is due to strong intermolecular hydrogen bonding.

The thermal stability of these polyamides was evaluated by thermogravimetric analysis (TGA). The TGA curves of these polymers are shown in

Figures 2 and 3, and thermal stability data are listed in Table 4.

Table 3. Softening points of polyamides.

Polymer	R	Softening point °C
II	-(CH <sub>2</sub> ) <sub>2</sub> -	210
III	-(CH <sub>2</sub> ) <sub>3</sub> -	192
IV	-(CH <sub>2</sub> ) <sub>6</sub> -	207

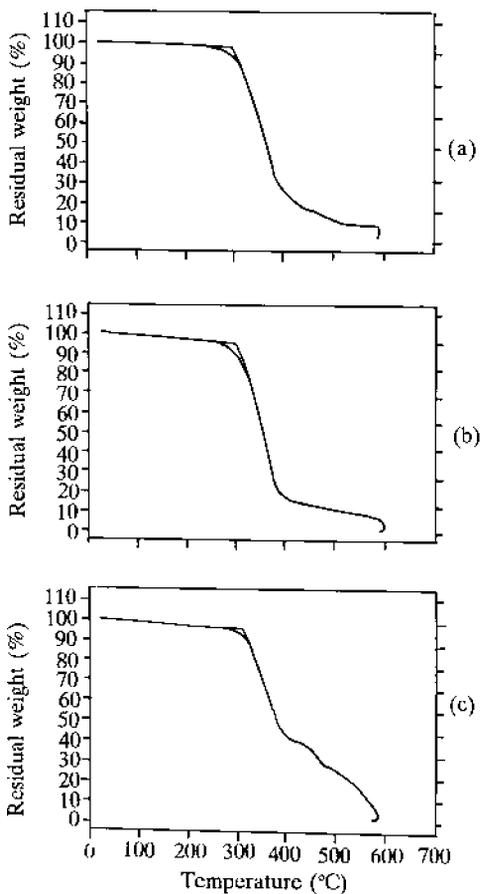


Fig.2. TGA curves in air: (a) polymer (II), (b) polymer (III), (c) polymer (IV).

Table 4. Thermal properties of polyamides.

Polymer	5% Weight losses		10% Weight losses		Residual Weight at 400 °C (%)	
	In air	In nitrogen	In air	In nitrogen	In air	In nitrogen
II	290	295	302	325	15.0	28.5
III	275	280	295	300	2.5	20.0
IV	270	290	300	320	60.0	44.0

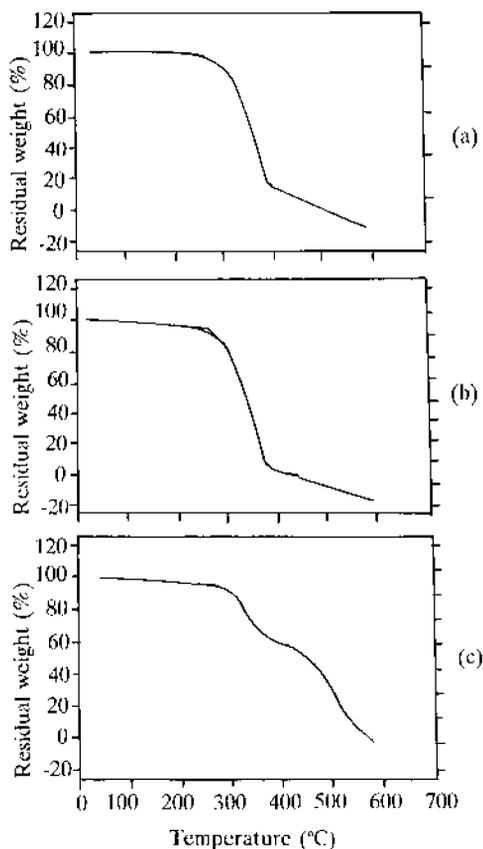


Fig.3. TGA curves in nitrogen: (a) polymer (II), (b) polymer (III), (c) polymer (IV).

An examination of the data reveals that the polymer IV is more thermally stable. This fact may

be attributed to the strong intermolecular hydrogen bonding.

In conclusion, the bulky benzo [k] fluoranthene unit can be readily introduced into the aromatic-aliphatic backbone. The resulted polyamides are thermally stable. Although the intrinsic viscosities are low in this case, higher viscosities may be obtained from the reaction of diacids or diacid chlorides of the monomer (I) with diamines. Such polycondensation reactions are under investigation.

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