

## Fast step-growth polymerization of 5-(3-acetoxynaphthoylamino)isophthalic acid with different diisocyanates under microwave irradiation

Zahra Rafiee\*

Department of Chemistry, Yasouj University, Yasouj 75918-74831, Islamic Republic of Iran

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### Abstract

The direct polycondensation reactions of diacid, 5-(3-acetoxynaphthoylamino)isophthalic acid with various aromatic and aliphatic diisocyanates such as 4,4'-methylene bis(4-phenylisocyanate), toluylene-2,4-diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate were carried out under microwave irradiation conditions. In order to compare this method with classical heating, the polymerization reactions were also performed under solution polycondensation conditions. The polymerization reactions occurred rapidly under microwave conditions and produced a series of polyamides containing pendent acetoxynaphthalamide group, with good yields and moderate inherent viscosities of 0.26-0.45 dL/g. The comparable yields and higher inherent viscosities were obtained by microwave irradiation versus thermal heating with substantial reduction in reaction time.

**Keywords:** Polyamide, Direct polycondensation, 5-(3-Acetoxynaphthoylamino)isophthalic acid, Diisocyanates

### 1. Introduction

Step-growth polymerization is among the first polymerizations, that studied using microwave heating technology and numerous examples have been reported in review articles and books [1-5]. Conventional polycondensation reactions involve, in many cases, the use of harsh conditions such as high temperatures and long reaction times, but they can be performed with great success with the assistance of microwave energy.

Microwave heating has been shown to dramatically reduce reaction times, increase product yields, and

enhance product purities by reducing unwanted side reactions compared to conventional heating methods [3,5]. The microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions [6]. Microwave irradiation facilitates the polarization of the molecules causing rapid reaction to occur.

Wholly aromatic polyamides (PAs) are high performance heat resistant polymers and have received particular attention [7]. Some of them are available for use as flame-resistant, high-strength,

\*.Corresponding Author: E-mail address: [z.rafiee@mail.yu.ac.ir](mailto:z.rafiee@mail.yu.ac.ir), [zahrarafiee2004@yahoo.com](mailto:zahrarafiee2004@yahoo.com); Tel.: +(98)7432223048

high modulus fibers and high efficiency semipermeable membranes as well as high performance plastics [8-10]. Due to stiffness of the polymer chains, and the strong molecular interactions through hydrogen bonding of amide groups, aromatic PAs, show limited solubility in organic solvents. The introduction of bulky pendent groups [11-14], packing-disruptive [15-17], flexible bonds and unsymmetrical or polar substituents [18,19] into the macromolecular chain has been established as a convenient approach to modify the properties of PAs without affecting their thermal stability.

In the present study, we successfully prepared a series of thermally stable PAs, by direct polycondensation of diacid, 5-(3-acetoxynaphthoylamino)isophthalic acid with various diisocyanates by a rapid and efficient methodology under microwave irradiation.

## 2. Experimental procedure

### 2.1. Materials and Methods

Reagents were purchased from Fluka, Aldrich and Riedel-deHaen AG. *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), pyridine (Py) and triethylamine (TEA) were dried over BaO and then were distilled under reduced pressure. The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900W). FTIR spectra were recorded on a Nicolet Impact 400D IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer at a concentration of  $0.5 \text{ g dL}^{-1}$  in DMF at  $25^\circ\text{C}$ . Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Stanton-650 TGA under  $\text{N}_2$  atmosphere.

### 2.2. Monomer synthesis

5-(3-Acetoxynaphthoylamino)isophthalic acid (1) as a diacid was prepared according to our pervious reported work [20].

### 2.3. Polymer synthesis

Method I: polymerization of diacid 1 with diisocyanates under conventional heating conditions  
General procedure for preparation of PAs: as an example for preparation of PA1aI, in a 25 mL round bottom flask a solution of diacid 1 ( $0.100 \text{ g}$ ,  $2.54 \times 10^{-4} \text{ mol}$ ) in  $0.20 \text{ mL}$  of NMP was added to a solution of hexamethylene diisocyanate (HDI) (2) ( $0.043 \text{ g}$ ,  $2.54 \times 10^{-4} \text{ mol}$ ) and dibutyltin dilaurate (DBTDL) ( $0.02 \text{ g}$ ,  $3.01 \times 10^{-5} \text{ mol}$ ) in  $0.20 \text{ mL}$  of dry NMP. The solution was stirred for 1 h at RT, 3 h at  $60^\circ\text{C}$ , 8 h at  $80^\circ\text{C}$ , and then it was heated gradually from  $100$  to  $120^\circ\text{C}$  during 4 h. Then, the reaction mixture was poured into  $30 \text{ mL}$  of methanol to precipitate the polymer. The solid was filtered off, dried to give  $0.130 \text{ g}$  (91%) of white PA1aI. This polymerization was also repeated using Py or TEA as a catalyst and without any catalyst, respectively.

Method II: polymerization of diacid 1 with diisocyanates under microwave irradiation

General procedure for preparation of PA1aII using microwave irradiation: as an example for preparation of PA1aII, into a porcelain dish diacid 1 ( $0.100 \text{ g}$ ,  $2.54 \times 10^{-4} \text{ mol}$ ) and  $0.20 \text{ mL}$  of NMP was placed. After the mixture was completely ground, DBTDL ( $0.02 \text{ g}$ ,  $3.01 \times 10^{-5} \text{ mol}$ ) was added, and the mixture was ground for 5 min, then a solution of HDI (2) ( $0.043 \text{ g}$ ,  $2.54 \times 10^{-4} \text{ mol}$ ) in  $0.20 \text{ mL}$  of dry NMP was added, and the mixture was ground again for additional 3 min. The reaction mixture was irradiated in the microwave oven for 3 min at 100% of power. The resulting product was isolated by the addition of  $30 \text{ mL}$  of methanol. It was then filtered and dried at  $80^\circ\text{C}$  for 8 h in vacuum; this yielded  $0.127 \text{ g}$  (89%) of white PA1aII. The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven in NMP, using Py and TEA as a catalyst and without catalyst, respectively. The other

PAs were prepared according to reaction time and reaction catalysts by the same procedure using other diisocyanates such as isophorone diisocyanate (IPDI) (3), toluene-2,4-diisocyanate (TDI) (4) and 4,4'-methylenebis(phenyl isocyanate) (MDI) (5).

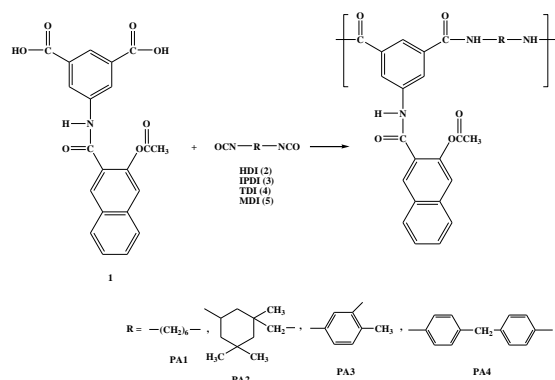
### 3. Results and discussion

#### 3.1. Monomer synthesis

Dicarboxylic acid 1 was synthesized in four steps according to our previous work [20].

#### 3.2. Polymer synthesis

Microwave irradiation has been shown not only to reduce reaction times, but often to provide higher yields of the desired products, as compared to conventional heating methods. We therefore conceived of a microwave-assisted and conventional heating synthesis of highly soluble aromatic PAs by polyamidation technique of aromatic dicarboxylic acid 1 with different diisocyanates in the presence of different catalysts and without catalyst (Scheme 1).



**Scheme 1.** Polycondensation reactions of monomer 1 with different diisocyanates.

The polymers were obtained in almost quantitative yields and possessed inherent viscosities ranging from 0.26 to 0.45 dL/g (Table 1). In method I, the reaction mixture was heated gradually from RT up to 120 °C. The resulting PAs were obtained in good yields and inherent viscosities. DBTDL was recognized to be the best catalysts (Table 1). In method II, the polymerization reactions were performed in NMP under microwave irradiation. The resulting polymers have good yields and moderate viscosities, especially in the case of DBTDL and no catalyst conditions (Table 2).

**Table 1.** Synthesis and some physical properties of PAs under conventional heating (Method I).

Polymer	Diisocyanate	Catalyst	Yield (%)	$\eta_{inh}^a$ (dL/g)
PA1aI	HDI	DBTDL	91	0.38
PA1bI	HDI	Py	87	0.31
PA1cI	HDI	TEA	82	0.31
PA1dI	HDI	No catalyst	81	0.36
PA2aI	IPDI	DBTDL	86	0.29
PA2bI	IPDI	Py	87	0.26
PA2cI	IPDI	TEA	86	0.27
PA2dI	IPDI	No catalyst	87	0.28
PA3aI	TDI	DBTDL	89	0.34
PA3bI	TDI	Py	84	0.32
PA3cI	TDI	TEA	81	0.31
PA3dI	TDI	No catalyst	80	0.30
PA4aI	MDI	DBTDL	88	0.41
PA4bI	MDI	Py	85	0.39
PA4cI	MDI	TEA	87	0.38
PA4dI	MDI	No catalyst	86	0.40

<sup>a</sup>Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

**Table 2.** Synthesis and some physical properties of PAs under microwave irradiation (Method II).

Polymer	Diisocyanate	Catalyst	Yield (%)	$\eta_{inh}^a$ (dL/g)
PA1aII	HDI	DBTDL	89	0.41
PA1bII	HDI	Py	83	0.35
PA1cII	HDI	TEA	85	0.36
PA1dII	HDI	No catalyst	86	0.38
PA2aII	IPDI	DBTDL	81	0.35
PA2bII	IPDI	Py	79	0.31
PA2cII	IPDI	TEA	78	0.29
PA2dII	IPDI	No catalyst	81	0.30
PA3aII	TDI	DBTDL	87	0.39
PA3bII	TDI	Py	85	0.37
PA3cII	TDI	TEA	88	0.35
PA3dII	TDI	No catalyst	86	0.31
PA4aII	MDI	DBTDL	89	0.45
PA4bII	MDI	Py	85	0.41
PA4cII	MDI	TEA	83	0.42
PA4dII	MDI	No catalyst	88	0.43

<sup>a</sup>Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

#### 3.3. Polymer characterization

The resulting polymers were characterized by FT-IR spectroscopy. The FT-IR spectra of resulting PAs showed the presence of the characteristic peaks for amide and ester functions and the absence of the

original peaks arising from the COOH and NCO groups in the corresponding diacid and diisocyanates precursors. FT-IR spectra of all polymers show the characteristic absorption peaks for the ester and amide at 1731 and 1668  $\text{cm}^{-1}$ , respectively, due to the symmetrical and asymmetrical carbonyl stretching vibrations. Band of amide N-H group appeared around 3343  $\text{cm}^{-1}$ . A strong band corresponding to C-N stretching can also be observed at 1312  $\text{cm}^{-1}$ .

### 3. 4. UV-vis absorption and fluorescence characteristics

The polymers exhibited maximum UV-vis absorption at 268 and 310 nm in DMF solution because of the  $\pi-\pi^*$  transitions of the aromatic chromophore (naphthalene). The fluorescence spectra of the monomer, and PAs were recorded in DMF. For example, in the case of the PA1aI, the polymer was excited at 268 nm, and emission fluorescence wavelengths were observed at 364 and 434 nm, respectively. All of these compounds show almost similar UV-vis and fluorescence spectra pattern.

### 3. 5. Solubility properties of PAs

Because of flexible group and amide and ester groups in polymers pendent group, these polymers are expected to have higher solubility. The solubility of PAs was tested quantitatively in various solvents. Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. All of the PAs are soluble in organic polar aprotic solvents such as DMF, DMAc, dimethyl sulfoxide (DMSO), NMP, and polar protic solvent such as  $\text{H}_2\text{SO}_4$  at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

### 3. 6. Thermal properties

The thermal properties of PA1aII and PA4aII were evaluated by means of TGA/DTG in a nitrogen atmosphere at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . Thermal stability of the polymers was studied based on 5 and 10% weight loss ( $T_5$ ,  $T_{10}$ ) of the polymers and residue at 600  $^{\circ}\text{C}$  (char yield). In addition, TGA data reveal that PAs are thermally stable up to 250  $^{\circ}\text{C}$ . The thermoanalysis data of these polymers are

summarized in Table 3. The temperature of 5% weight loss for PA1aII was 284  $^{\circ}\text{C}$ , the temperature of 10% weight loss was 305  $^{\circ}\text{C}$ , and the residual weight for this polymer at 600  $^{\circ}\text{C}$  was 34% under nitrogen atmosphere. According to Table 3, it is clear that the PA4aII (based on MDI) has higher thermal stability than PA1aII (based on HDI). It could be pertained to aromatic, rigid structure of diisocyanate for PA4aII compared to aliphatic, flexible structure of diisocyanate for PA1aII. According to these data, it can be concluded that the resulting polymers have moderate thermally stability.

**Table 3.** Thermal properties of PA1aII and PA4aII.

Polymer	Decomposition Temperature ( $^{\circ}\text{C}$ )		Char Yield (%) <sup>c</sup>
	$T_5^a$	$T_{10}^b$	
PA1aII	284	305	34
PA4aII	298	327	37

<sup>a,b</sup>Temperatures at which 5% and 10% weight loss were recorded by TGA at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere, respectively.

<sup>c</sup>Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600  $^{\circ}\text{C}$ .

## 4. Conclusion

In this study, a series of PAs containing acetoxynaphthalamide pendent group were prepared by two different methods including microwave-assisted polycondensation and solution polycondensation reactions of an equimolar mixture of dicarboxylic acid 1 with different diisocyanates in the presence of small amount of NMP and several catalysts. The best inherent viscosity was obtained from the reaction of monomer 1 with MDI 5 by both methods in the presence of DBTDL and no catalyst conditions. The resulting polymers have inherent viscosities in the range of 0.26-0.45 dL/g. Good yields and very short reaction times are the main aspects of using microwave for polymerization. On the other hand, the introduction of bulky side chains should disturb interchain hydrogen bonding, inherent macromolecular rigidity, and diminish packing efficiency and crystallinity. The outcome offered herein also expresses obviously that the acetoxynaphthalamide linkage in the polymer side

chain outstandingly enhanced the solubility and thermal stability of the polymers.

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