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Microwave-induced synthesis of chiral polyamides containing phthalimide, L-alanine and benzamide linkages

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Abstract: An aromatic optically active dicarboxylic acid monomer, 5-[4-(2-phthalimidiylpropanoylamino)benzoylamino] isophthalic acid was prepared in five steps in high yield and purity. A series of organosoluble, thermally stable and optically active polyamides (PA)s containing pendent groups of phthalimide, L-alanine and benzamide have been successfully synthesized under microwave irradiation. Excellent yields and very short reaction time were the main characteristics of this method. The same polymerization reactions were also carried out by conventional thermal heating and the results are compared. The resulting PAs had inherent viscosity in the range of 0.30-0.51 dL g^{-1}. All of the these polymers are readily dissolved in various solvents such as *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide and *N,N*-dimethylformamide. Thermogravimetric analysis demonstrated that the 10% weight-loss temperatures in nitrogen were 378 and 394 °C for selected two PAs. All of these polymers showed optical rotation which is due to successful insertion of L-alanine in the structure of chiral diacid monomer.

Keywords: Polyamide, Direct polycondensation, 5-[4-(2-Phthalimidiylpropanoylamino)benzoylamino]isophthalic acid, Diisocyanates.

Introduction

Microwave irradiation is widely accepted as effective and non-conventional energy source for performing chemical reactions. Advantages that derived from the exploitation of microwave irradiation as heating source could comprise remarkable merits of reduced reaction time, improved yields, suppressed side reactions, decreased environmental pollutions and safe operations [1-5]. Therefore, a large and continuing survey has been made throughout nearly all classes of thermal reactions for improvements on microwave heating.

Isocyanates are highly reactive compounds that have been extensively used for the synthesis of a large variety of organic derivatives. The use of diisocyanates in the field of polymer chemistry has led to the successful synthesis of many polymers with versatile properties [6-8].

Wholly aromatic polyamides (aramids) are recognized as high-performance polymeric materials because of their high temperature stability, good chemical resistance and excellent mechanical properties [9,10]. However, they have limited processability owing to insolubility in most organic solvents and high glass transition and softening temperatures, which restrict their applications. Thus numerous investigations have been made to modify the chemical structure of these polymers, in order to improve their solubility and processability, while preserving their exceptional properties [11-15]. In preceding studies, it has been described that introducing bulky pendent groups is a valuable

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approach for enhancing solubility, without affecting thermal properties of polymers. The polyamides with a *N*-phthalimide side substituent have been reported and found to be superior to the unsubstituted polyamides in both thermal stability and solubility [13,15].

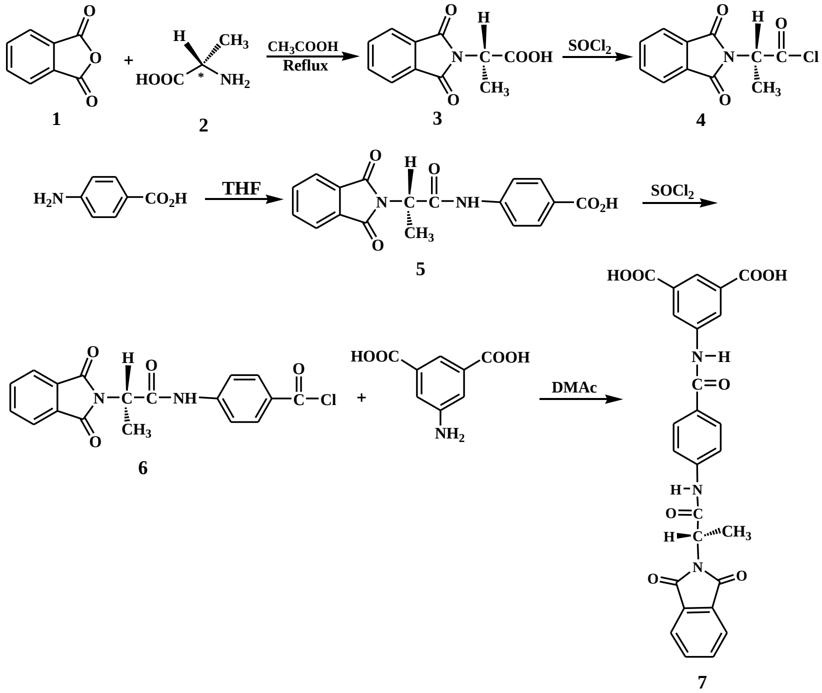
Synthesis of optically active polymers is an important field in polymer science as they find wide variety of potential uses based on the chiral structure. An important application of these polymers is chiral recognition. This ability of chiral polymers has been utilized in various forms of catalytic and separation chemistry [16,17]. Optically active polyamides are promising materials where chiro-optical effects can be combined with good mechanical and thermal properties [18]. On the other hand, incorporation of α-amino acid moieties along the polyamide chain could be an effective strategy for enhancing the biodegradability [19].

In the present study, we successfully prepared a series of thermally stable polyamides via direct polycondensation of dicarboxylic acid, 5-[4-(2-phthalimidiylpropanoylamino)benzoylamino]isophthalic acid with different diisocyanates by a fast and efficient method under microwave irradiation.

Results and discussion

Monomer synthesis:

As shown in Scheme **1**, dicarboxylic acid 7 was prepared in five steps according to our previous work [5].



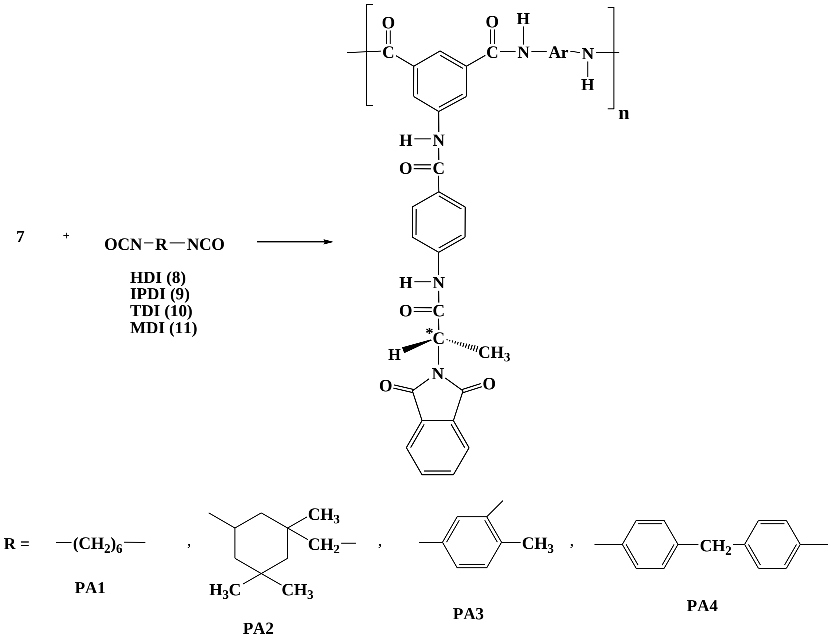
Scheme 1: Synthesis of monomer 7.

Polymer synthesis:

Microwave-assisted polycondensation as well as solution polycondensation of an equimolar mixture of monomer 7 with different aromatic and aliphatic diisocyanates 8-11 were performed in the presence of different catalysts, as shown in Scheme **2**. The reaction of diisocyanates with diacids initially forms anhydrides linkages that are not stable under the reaction conditions, and CO_2 was evolved to give stable amide linkages. The polymers were obtained in almost quantitative yields and possessed inherent viscosities ranging from 0.30 to 0.51 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 catalyst (Table **2**).

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 function 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 at around 1777-1668 cm^{-1}for the the symmetrical and asymmetrical carbonyl stretching vibrations of carbonyl groups. Band of amide N-H group appeared around 3342 cm^{-1}. A strong band corresponding to C-N stretching can also be observed at 1310 cm^{-1}.



Scheme 2: Polycondensation reactions of monomer 7 with different diisocyanates.

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

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh}^{a} (dL/g)
PA1aI	HDI	DBTDL	83	0.42
PA1bI	HDI	Py	81	0.39
PA1cI	HDI	TEA	80	0.39
PA1dI	HDI	No catalyst	82	0.40
PA2aI	IPDI	DBTDL	79	0.32
PA2bI	IPDI	Py	76	0.31
PA2cI	IPDI	TEA	77	0.30
PA2dI	IPDI	No catalyst	76	0.30
PA3aI	TDI	DBTDL	81	0.36
PA3bI	TDI	Py	78	0.34
PA3cI	TDI	TEA	79	0.34
PA3dI	TDI	No catalyst	80	0.35
PA4aI	MDI	DBTDL	83	0.43
PA4bI	MDI	Py	81	0.41
PA4cI	MDI	TEA	82	0.40
PA4dI	MDI	No catalyst	81	0.41

[a]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 (%)	η_{inh}^{a} (dL/g)
PA1aII	HDI	DBTDL	85	0.48

PA1bII	HDI	Py	83	0.44
PA1cII	HDI	TEA	84	0.40
PA1dII	HDI	No catalyst	84	0.47
PA2aII	IPDI	DBTDL	83	0.38
PA2bII	IPDI	Py	80	0.36
PA2cII	IPDI	TEA	81	0.35
PA2dII	IPDI	No catalyst	82	0.36
PA3aII	TDI	DBTDL	84	0.42
PA3bII	TDI	Py	83	0.39
PA3cII	TDI	TEA	84	0.38
PA3dII	TDI	No catalyst	81	0.39
PA4aII	MDI	DBTDL	84	0.51
PA4bII	MDI	Py	84	0.47
PA4cII	MDI	TEA	82	0.46
PA4dII	MDI	No catalyst	83	0.46

[a] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

Solubility properties of Pas:

Because of flexible group and amide groups in polymers pendent group, these polymers are expected to have higher solubility. The solubility of PAs was tested quantitatively in various solvents. 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 H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

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 °C/min. Thermal stability of the polymers was studied based on 5 and 10% weight loss (T5, T10) of the polymers and residue at 600 °C (char yield). In addition, TGA data reveal that PAs are thermally stable up to 330 °C. The thermoanalysis data of these polymers are summarized in Table **3**. The temperature of 5% weight loss for PA1aII was 355 °C, the temperature of 10% weight loss was 378 °C, and the residual weight for this polymer at 600 °C was 38% 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 are rather thermally stable.

Table 3: Thermal properties of PA1aII and PA4aII.

Polymer	Decomposition Temperature (°C)		Char Yield (%)[c]
	T_5[a]	T_{10}[b]	
PA1aII	355	378	38
PA4aII	368	394	41

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.
[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.
[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 °C under nitrogen atmosphere.

Conclusion

In this study, a series of PAs containing phthalimide, L-alanine and benzamide pendent groups were prepared by two different methods such as microwave-assisted polycondensation and solution polycondensation reactions of an equimolar mixture of dicarboxylic acid 7 with different diisocyanates in the presence of small amount of NMP and several catalysts. The best results were obtained from the reaction of monomer 7 with MDI 11 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 phthalimide, L-alanine and benzamide linkage in the polymer side chain outstandingly enhanced the solubility and thermal stability of the polymers.

Experimental

Materials:

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.

Techniques:

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 (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 g dL^{-1} in DMF at 25 °C. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Stanton-650 TGA under nitrogen atmosphere.

Monomer synthesis:

5-[4-(2-Phthalimidiyl propanoylamino)benzoyl amino] isophthalic acid (7) was prepared (Scheme **1**) according to our previous work [5].

Polymer synthesis:

Method I: polymerization of diacid 7 with diisocyanates under conventional heating conditions

General procedure for preparation of polyamides (PA)s: as an example for preparation of PA1AI, in a 25 mL round bottom flask a solution of diacid 7 (0.100 g, 1.94×10^{-4} mol) in 0.20 mL of NMP was added to a solution of hexamethylene diisocyanate (HDI) (8) (0.033 g, 1.94×10^{-4} mol) and dibutyltin dilaurate (DBTDL) (0.02 g**,** 3.01×10^{-5} mol) in 0.20 mL of dry NMP. The solution was stirred for 1 h at RT, 3 h at 60 °C, 8 h at 80 °C, and then it was heated gradually from 100 to 120 °C during 4 h. Then, the reaction mixture was poured into 30 mL of methanol to precipitate the polymer. The solid was filtered off, dried to give 0.110 g (83%) 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 7 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 7 (0.100 g, 1.94×10^{-4} mol) and 0.20 mL of NMP was placed. After the mixture was completely ground, DBTDL (0.02 g**,** 3.01×10^{-5} mol) was added, and the mixture was ground for 5 min, then a solution of HDI (8) (0.033 g, 1.94×10^{-4} mol) in 0.20 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 mL of methanol. It was then filtered and dried at 80 °C for 8 h in vacuum; this yielded 0.113 g (85%) 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) (9), toluene-2,4-diisocyanate (TDI) (10) and 4,4'-methylenebis(phenyl isocyanate) (MDI) (11).

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