

Facile Synthesis of Novel Optically Active Poly(amide-imide)s Derived from *N,N*-(Pyromellitoyl)-bis-*l*-alanine Diacid Chloride, Tetrahydropyrimidinone and Tetrahydro-2-thioxopyrimidine by Microwave-assisted Polycondensation

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ABSTRACT

Seven new optically active poly(amide-imide)s (**3a-g**) were synthesized by microwave assisted polycondensation of *N,N*-(pyromellitoyl)-bis-*l*-alanine diacid chloride (1) with seven different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a-g**) by using a domestic microwave oven. The polycondensation reactions were carried out in the presence of a small amount of a polar organic medium that acts as a primary microwave absorber. Suitable organic media was *o*-cresol. The polycondensation proceeded rapidly, compared with the conventional melt polycondensation and solution polycondensation and it was almost completed within 10 min giving a series of poly(amide-imide)s (**3a-g**) with inherent viscosities about 0.22-0.42 dL/g. The resulting poly(amide-imide)s were obtained in high yield and were optically active and thermally stable. All of the above compounds were fully characterized by means of FTIR spectroscopy, elemental analysis, inherent viscosity (η_{inh}), solubilities test, and specific rotation. Thermal properties of the poly(amide-imide)s were investigated using thermal gravimetric analysis (TGA).

Key Words:

microwave-assisted rapid polycondensation; optically active polymers; poly(amide-imide)s; tetrahydropyrimidinone; and tetrahydro-2-thioxopyrimidine compounds.

INTRODUCTION

Poly(amide-imide)s, PAIs, are a class of high-performance polymers, which show excellent mechanical and thermal properties and are also solvent resistant [1,2]. There are numerous applications for them, which include electronic wire enam-

el, adhesives, injection-moulding and extrusion products and membranes [3-6]. They inherit desirable characteristics from both polyamide and polyimides and possess good thermal properties compared to polyamide, and better melt process-

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ability than polyimides. Many approaches have been investigated in attempting to improve the solubility of aromatic polyimides including the addition of pendant groups to polymeric backbone [7-8] and incorporation of bulky [9-11] or flexible [12-13] and heterocycles [14-16] unit within the parent chain.

The synthesis and application of optically active polymers are the newly considerable topics, which have been paid more attention recently. Because polymers with chiral structures are biologically very important. Recently, we have synthesized optically active polymers by different methods [17-23].

In the present article, we will describe the synthesis and characterization of new optically active PAIs (**3a-g**) from the polycondensation reactions of *N,N*-(pyromellitoyl)-bis-*l*-alanine diacid chloride (1) with seven different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine (**2a-g**) as a heterocycles unit using a domestic microwave oven.

Monocyclic six-member ring nitrogen heterocycles such as tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds are an extremely important class of compounds that occur in a wide variety of natural products such as purine, caffeine, nucleic acids (DNA, RNA), uric acid, and synthetic products [24].

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Merck Chemical Co. (Germany).

Techniques

Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities (η_{inh}) were measured by a standard procedure using a Technico Regd. Trad. Merck Viscometer. Specific rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA 4000 System under N_2 atmosphere at a rate of $100^\circ\text{C}/\text{min}$. Elemental analyses were performed by Arak

Petrochemical Company, Arak, Iran. As the source of microwave irradiation, we used a Samsung domestic microwave oven (2450 MHz, 900W) for carrying out the polycondensation reactions.

Monomer Synthesis

Tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a-g**) were prepared according to the Biginelli method [25] that has been shown in Scheme I. *N,N*-(Pyromellitoyl)-bis-*l*-alanine diacid chloride (1) was prepared by procedure reported elsewhere [26].

Polymer Synthesis

PAIs (**3a-g**) were synthesis by a typical procedure shown in Scheme II.

An equimolar mixture of optically active diacid chloride (1) (0.5 mmol) and tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a-g**) (0.5 mmol) were placed in a reaction vessel and the mixture was grounded until fine powder formed. Then 0.5 mL of *o*-cresol was added to the mixture and mixed up until homogeneous solution formed. The PAIs were then synthesized by microwave assisted polycondensation reactions by placing in microwave oven at full power for 10 min. The reaction mixture was poured into 50 mL of methanol. Then the resulting polymer was filtered off, and dried at 80°C for 8 h under a vacuum.

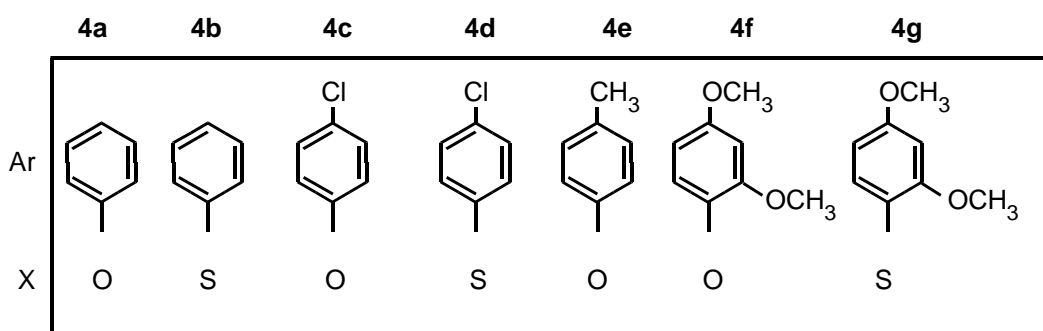
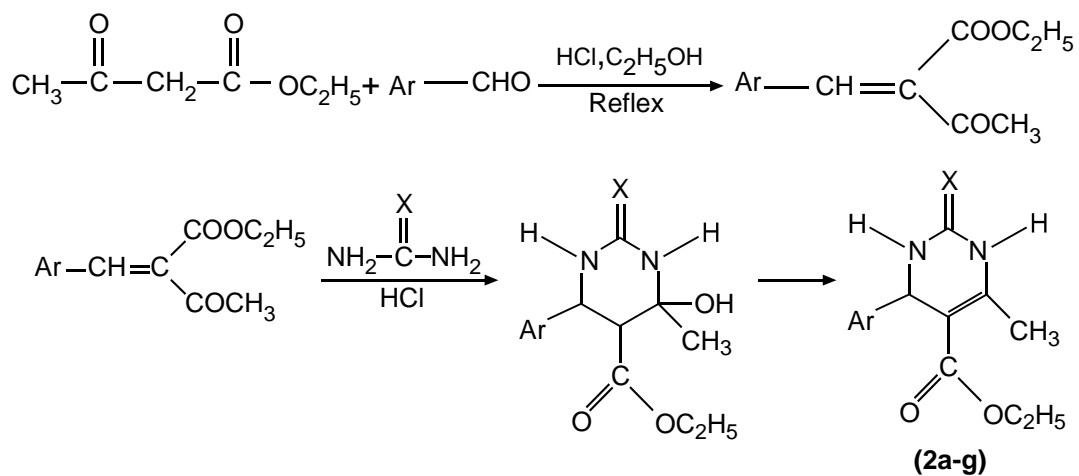
RESULTS AND DISCUSSION

Monomer Synthesis

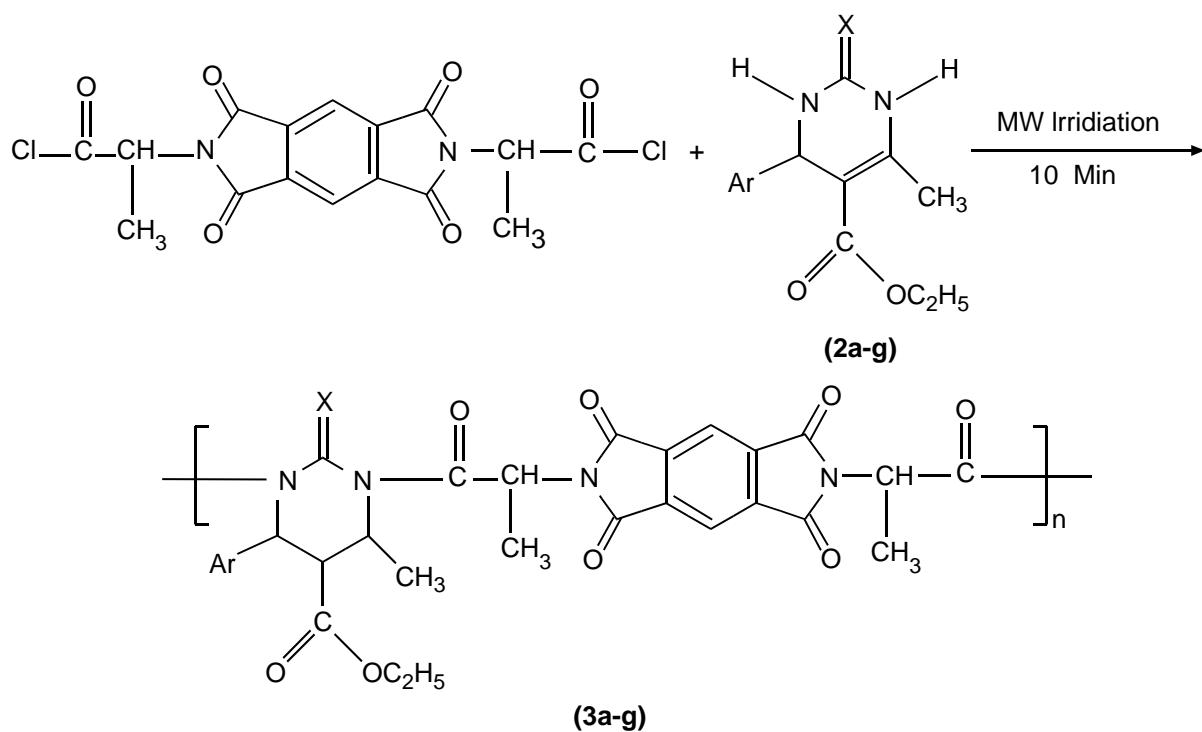
4-Aryl-3,4-dihydro-2(1H)-pyrimidinone esters of type (**2a-g**) (Biginelli compounds) represent a heterocyclic system with remarkable pharmacological efficiency [27]. The most straightforward protocol to synthesize of these compounds (**2a-g**) involves the one-pot condensation of a β -keto ester with an aryl aldehyde and urea or thiourea derivative under strongly acidic condition (Scheme I)[25].

Polymer Synthesis

Poly(amide-imide)s (**3a-g**) were synthesized by microwave assisted polycondensation reactions of an equimolar mixture of monomer (1) with seven different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds (**2a-g**) in *o*-cresol as organic solvent by using a domestic microwave oven as



Scheme I



Scheme II

shown in Scheme II. The *o*-cresol was used as polar organic medium that acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers which allows to induce effective homogeneous heating of the reaction mixture and thereby subsequent polycondensation reaction leading to the polymer formation. The optimum period of reaction time (irradiation time) was found to be 10 min and below this time will give polymers with lower inherent viscosities and above this time the materials will degradate.

Polymer Characterization

Synthesis and some physical properties of poly(amide-imide)s (**3a-g**) are summarized in Table 1. These polymers have inherent viscosities in a range of 0.22-0.42 dL/g. Poly(amide-imide)s derived from monomer (1) may range in colour from cream or off-white to pale-yellow, except polymers (**3b**), (**3d**) and (**3g**), which have an intense, orange colour and pale-orange colour, respectively. According to this deep colour, the polarized light could not transmit through the polymer solution, and therefore their optical rotations were undefined (Table 1). The other resulting polymers show optical rotation and are optically active.

The structures of these polymers were confirmed as poly(amide-imide)s by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PAIs (**3c**) was shown in Figure 1. The polymer show absorption bands around 1780-1670 cm^{-1} due to carbonyl of amide, imide and ester linkages. Absorption bands around 1390-1370 cm^{-1} and 750-710 cm^{-1} show the presence of the imide heterocycle in this polymer. The absorption bands between 1300-1000 cm^{-1} due to

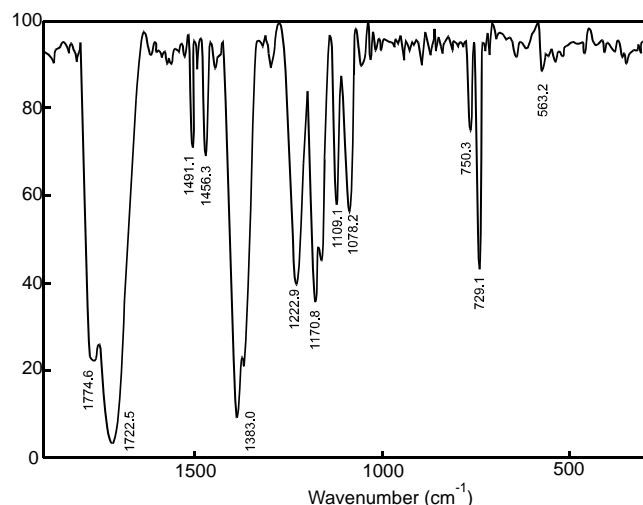


Figure 1. FTIR Spectrum of polymer **3c**.

Table 2. FTIR Spectra of PAIs (**3a-g**).

Polymer	Spectral data
3a	FTIR(KBr): 1772(s,sh), 1724(s,br), 1496(w), 1458(w), 1383(s,br), 1370(s,sh), 1222(m), 1170(m), 1109(w), 1078(w), 752(w), 727(w) cm^{-1} .
3b	FTIR(KBr): 1764(s,sh), 1724(s,br), 1647(w), 1491(w), 1458(w), 1384(s,br), 1370(s,sh), 1222(s), 1170(m), 1109(m), 1080(m), 752(w), 729(m) cm^{-1} .
3c	FTIR(KBr): 1774(s,sh), 1722(s,br), 1491(w), 1458(w), 1383(s,br), 1370(s,sh), 1222(s), 1170(s), 1109(m), 1078(m), 750(w), 729(m) cm^{-1} .
3d	FTIR(KBr): 1764(s,sh), 1724(s,br), 1550(w), 1494(m), 1460(m), 1383(s, br), 1370(s,sh), 1222(s), 1172(m), 1109(m), 1078(m), 1020(w), 752(w), 729(m) cm^{-1} .
3e	FTIR(KBr): 1774(s,sh), 1724(s,br), 1496(w), 1458(w), 1383(s,br), 1371(s,sh), 1222(s), 1170(m), 1111(m), 1077(m), 750(w), 729(m) cm^{-1} .
3f	FTIR (KBr): 1768(s,sh), 1724(s,br), 1491(m), 1458(w), 1383(s,br), 1370(s,sh), 1222(s), 1170(m), 1112(m), 1089(m), 750(w), 729(m) cm^{-1} .
3g	FTIR (KBr): 1764(s, sh), 1724(s, br), 1647(w), 1491(m), 1458(w), 1384(s,br), 1371(s,sh), 1222(s), 1172(s), 1109(m), 1080(m), 752(w), 729(m) cm^{-1} .

Table 1. Synthesis and some physical properties of PAIs (**3a-g**).

Heterocyclic monomer	Polymer	Yield(%)	η_{inh} (dL/g) ^a	$[\alpha]_{\text{D}}^{25\text{b}}$
2a	3a	78	0.22	-14.00
2b	3b	75	0.30	-
2c	3c	80	0.42	-9.00
2d	3d	77	0.30	-
2e	3e	87	0.23	-12.00
2f	3f	82	0.38	-11.00
2g	3g	78	0.35	-

^{a,b} Measured at a concentration of 0.5 g/dL in DMF at 25°C.

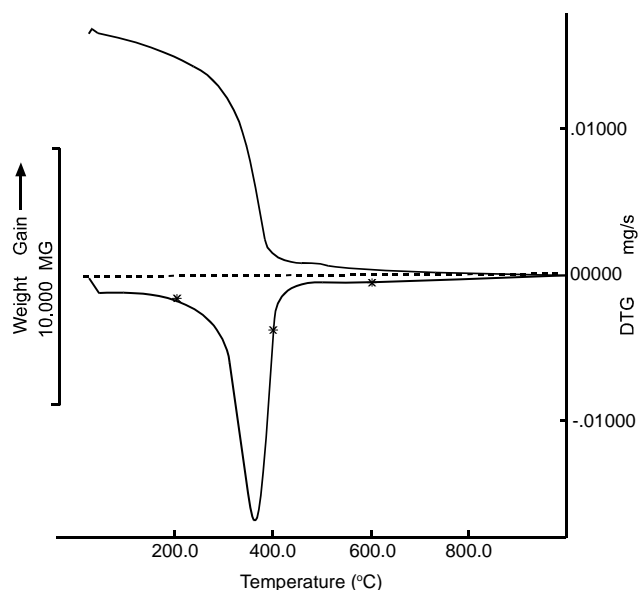


Figure 2. TGA and DTG Thermograms of polymer **3a**.

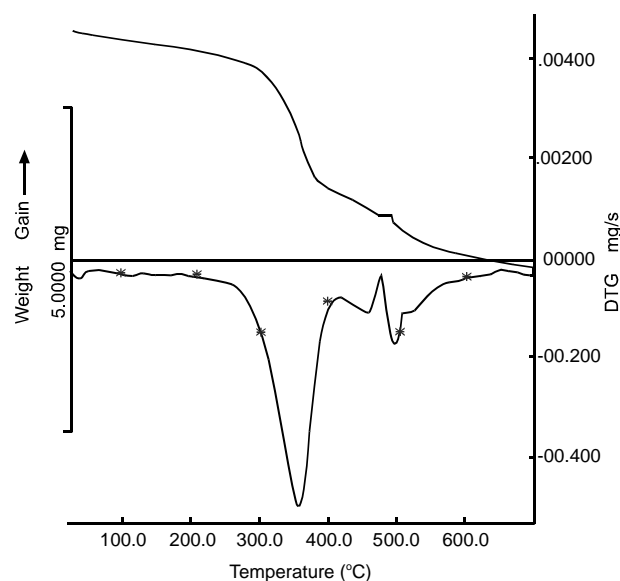


Figure 3. TGA and DTG Thermograms of polymer **3c**.

C-O of ester linkage in this polymer (Table 2).

The results of elemental analysis were in good agreement with the calculated values (Table 3).

The solubility characteristics of poly(amide-imide)s (**3a-g**) were investigated as 0.01 g of polymer-ic sample in 2 mL of solvent. It was found that all of the polymers dissolved in organic solvents such as NMP,

DMF, DMAc, DMSO and acetone at room temperature were insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Thus an increase in the solubility was resulted from incorporation of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine moieties into polymer backbone.

Table 3. Elemental analysis of aromatic poly(amide-imide)s **3(a-g)**.

Polymer	Formula		C (%)	H (%)	N (%)
3a	$C_{30}H_{24}N_4O_9$ (584) _n	calcd	61.64	4.10	9.58
		found	62.4	4.7	8.2
3b	$C_{30}H_{24}N_4O_8S$ (600) _n	Calcd	60.00	4.00	9.33
		found	62.1	4.3	8.4
3c	$C_{30}H_{23}N_4O_9Cl$ (618.5) _n	calcd	58.20	3.71	9.05
		found	60.2	4.6	8.0
3d	$C_{30}H_{23}N_4O_8ClS$ (634.5) _n	calcd	56.73	3.62	8.82
		found	57.6	4.2	7.8
3e	$C_{31}H_{26}N_4O_9$ (598) _n	calcd	62.20	4.34	9.36
		found	63.5	4.7	7.9
3f	$C_{32}H_{28}N_4O_{11}$ (644) _n	Calcd	59.62	4.33	8.69
		found	58.1	4.0	7.5
3g	$C_nH_{28}N_4O_{10}S$ (660) _n	calcd	58.18	4.24	8.48
		found	57.0	5.1	7.2

Table 4. Solubilities of PAIs **3(a-g)**.

Solvent	3a	3b	3c	3d	3e	3f	3g
DMAc	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+
THF	-	-	-	-	-	-	-
MeOH	-	-	-	-	-	-	-
EtOH	-	-	-	-	-	-	-
CHCl ₃	-	-	-	-	-	-	-
CH ₂ Cl ₂	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-

(+) Soluble at room temperature, (-) Insoluble at room temperature.

Table 5. Thermal behaviour of aromatic PAIs.

Polymer	Decomposition temperature (°C)		Char yield (%) ^b
	T ₅ ^a		
3a	205-210		8.5
3c	210-215		7.0

(a) Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N₂; (b) Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in N₂.

Thermal Properties

The thermal properties of PAIs (**3a**, **3c**) were evaluated by means of TGA/DTA in nitrogen atmosphere. All of the polymers show similar decomposition behaviour (Figures 2-3). For (**3a**) it started to decompose at 205°C, lost 5% of its weight due to decomposition by 210°C and by 600°C only had 8.5% of original weight. For (**3c**) it started to decompose at 210°C, had lost 5% of its weight due to decomposition by 215°C and by 600°C only had 7.0% of original weight (Table 5).

CONCLUSION

Seven novels optically active PAIs (**3a-g**) were synthesized by microwave assisted polycondensation reaction using the optically active monomer (**1**) with seven different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine (**2a-g**) as a heterocycles unit. These aromatic PAIs are optically active and are soluble in various organic solvents. The introduction of

tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine moieties into the backbone increased solubility of these polymers. These resulting novel polymers have the potential to be used in column chromatography technique for the separation of the enantiomeric mixtures. Furthermore, the above results demonstrate that microwave heating is an efficient method (sh

We are currently using this method for synthesis of novel polymers and modification of polymers.

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