

Using Microwave Irradiation to Prepare New Poly(amide-imide)s Containing Tetrahydropyrimidinone, Tetrahydro-2-thioxopyrimidine, and Trimellitic Rings in Their Main Chains: Synthesis and Characterization

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Abstract: Under irradiation in a microwave oven, six novel poly(amide-imide)s containing tetrahydropyrimidinone, tetrahydro-2-thioxopyrimidine moieties and trimellitic rings in their main chains were synthesized through the polycondensation reaction of *N,N'*-(4,4'-diphenylether)bis(trimellitimide) diacid chloride with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine in the presence of a small amount of a polar organic medium, such as *o*-cresol. The polycondensation proceeded rapidly and completed within 7-9 min, producing a series of new poly(amide-imide)s in high yield that showed inherent viscosities in the range 0.33-0.52 dL/g. These poly(amide-imide)s were characterized by elemental analysis, viscosity measurement, thermal gravimetric analysis, solubility test, and FT-IR spectroscopy. All of the polymers were soluble at room temperature in polar solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethylsulfoxide, tetrahydrofuran, and *N*-methyl-2-pyrrolidone.

Keywords: poly(amide-imide)s, polycondensation, microwave irradiation, characterization, thermally-stable polymers.

Introduction

Recently microwave irradiation has received growing application in organic synthesis for optimization and acceleration of chemical reactions.¹⁻⁴ In some cases microwave heating is superior to thermal heating and was shown to increase reaction rates, selectivity and yields of target products and it reduce tarring.⁵ Microwave energy is being investigated as a method to process resins, such as epoxides,^{6,7} polyesters,⁸ polyurethanes⁹ and more recently polyimides^{10,11} due to the advantages of shorter processing time, improved energy utilization, and the potential for lower processing temperature and improved product uniformity.¹² Recently we have used the microwave irradiation for the synthesis of polyamides, poly(amide-imide)s and poly(ester-imide)s.¹³⁻¹⁸ Aromatic polyimides are well known as high-performance polymeric materials because of their excellent thermal stability as well as the balanced mechanical and electrical properties and have been used in the fields of adhesives, composites, fibers, films and electrical materi-

als.^{19,20} However aromatic polyimides are difficult to process because of their high softening temperature and limited solubility in organic solvents. In order to overcome these weak points some methods are used such as addition of flexible linkages in the main chain,²¹ introduction of subsistent groups,²² a flexible spacer²³ and hetrocyclic moieties in the main chain.²⁴ Synthesis of poly(amide-imide)s with hetrocyclic moieties is one of the best methods. In our pervious works, we used this method for synthesis of a series of new poly(amide-imide)s with the demanded properties. In this article, we prepare a series of novel poly(amide-imide)s containing trimellitic rings and tetrahydropyrimidinone and tetrahydro-2-thioxo-pyrimidine moieties from the polycondensation reaction of *N,N'*-(4,4'-diphenylether) bistrimellitimide diacid chloride **4** with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds **5a-f** under microwave irradiation.

Experimental

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Merck Chemical Co. (Germany). Fourier transform infrared

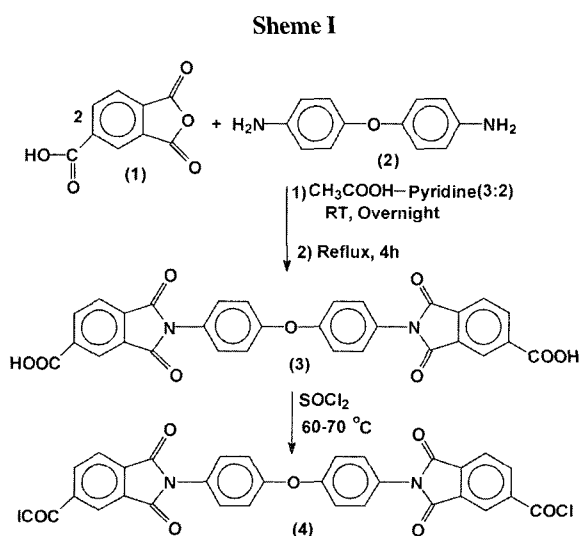
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(FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). FT-IR spectra of solids were measured using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, I. R. Iran. A Samsung domestic microwave oven (2,450 MHz, 900 W) was used for the polycondensation reactions.

Monomer Synthesis. *N,N'*-(4,4'-diphenylether) bistrimellitimidic diacid chloride **4** was prepared according to a typical procedure that was shown in Scheme I.²⁵

***N,N'*-(4,4'-diphenylether) Bistrimellitimidic Diacid Chloride 4.** Into a 250 mL round-bottom flask (3.84 g, 20 mmol) of trimellitic dianhydride **1**, (2.00 g, 10 mmol) of 4,4'-diaminodiphenyl ether **2**, 80 mL of mixture of acetic acid and pyridine (3:2) and a stirring bar were placed. The mixture was stirred at room temperature for overnight and then refluxed for 4 h. The solvent was removed under reduced pressure and the residue was dissolved in 100 mL of cold water, then 5 mL of concentrated HCl was added. The solution was stirred until a yellow precipitate was formed, then the precipitate was filtered off and dried, to give 4.95 g (90.3%) of yellow crystal compound **3**. mp $392\text{--}394^\circ\text{C}$ (Lit. 380),²⁵ FT-IR (KBr): 3500-2800 (m,br), 1780 (w, sh), 1730-1700 (s, br), 1608 (m), 1506(s), 1425 (w), 1392 (s), 1307 (s), 1300 (m), 1257-1200 (s, br), 1168 (m), 1118 (m), 1100 (m), 927 (w), 883 (w), 827 (m), 727 (m) cm^{-1} . Analysis: calculated for $\text{C}_{30}\text{H}_{16}\text{N}_2\text{O}_9$; C, 65.71%; H, 2.92%; N, 5.10%; found: C, 65.50%; H, 3.10%; N, 4.80%.

***N,N'*-(4,4'-diphenylether) Bistrimellitimidic Diacid**



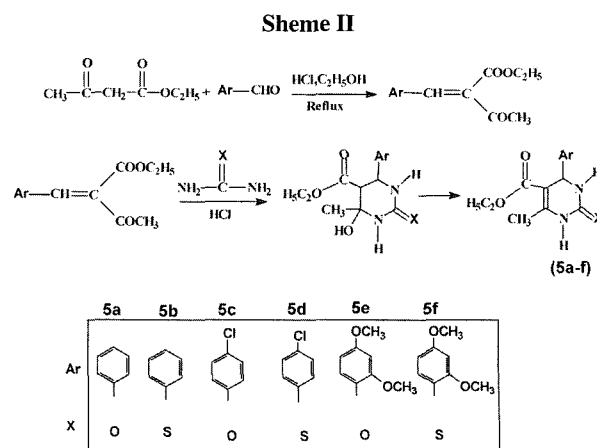
Chloride 4. Into a 100 mL round-bottom flask were placed (3.00 g, 5.47 mmol) of *N,N'*-(4,4'-diphenylether) bistrimellitimidic diacid chloride **3** and 20 mL of thionyl chloride. The mixture was heated on an oil bath up to 60°C , until the suspension mixture was converted to a clear solution. Then, the solution was stirred for overnight at room temperature. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry *n*-hexane two times to leave 3.09 g (96.5%) of yellow crystals of compound **4**. mp $270\text{--}273^\circ\text{C}$, FT-IR (KBr): 1780 (m, sh), 1757 (s, br), 1724 (s, br), 1504 (s), 1425 (w), 1379 (s), 1240-1220 (s, br), 1151 (m), 1111 (m), 1087 (m), 968 (m), 850-830 (m), 729 (m), 690 (m) cm^{-1} . Analysis: calculated for $\text{C}_{30}\text{H}_{14}\text{N}_2\text{O}_7\text{Cl}_2$; C, 61.56%; H, 2.39%; N, 4.78%; found: C, 61.40%; H, 2.50%; N, 4.50%.

Tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds **5a-f** were prepared according to the Biginelli condensation (Scheme II).²⁶

Polymer Synthesis. Poly(amide-imide)s **6a-f** were synthesized by a typical procedure shown in Scheme III. An equimolar mixture of diacid chloride **4** (0.585 g, 1.0 mmol) and tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds **5a-f** (1.0 mmol) were placed in a porcelain dish and the mixture was grounded until fine powder was formed. Then 0.7 mL of *o*-cresol was added to the mixture and mixed up until homogeneous solution formed. Then the reaction mixture was irradiated in microwave oven at full power for 7-9 min. The reaction mixture was poured into 50 mL of methanol and the resulting polymer was filtered off and dried at 80°C for 12 h under vacuum.

Results and Discussion

Monomer Synthesis. 4-Aryl-3,4-dihydro-2(1H)-pyrimidinone esters of type **5a-f** (Biginelli compounds) represent a heterocyclic system with remarkable pharmacological efficiency.²⁶ The most straightforward protocol to synthesize of these compounds **5a-f** involves the one-pot condensation of a β -keto ester, with an aryl aldehyde, and urea or thiourea derivative under strongly acidic condition (Scheme II).²⁷



Polymer Synthesis. According to our previous results,¹³⁻¹⁸ poly(amide-imide)s **6a-f** were synthesized by microwave assisted polycondensation reactions of an equimolar mixture of monomer **4** with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine **5a-f** as shown in Scheme III. The *o*-cresol was used as a polar organic medium that acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers. This allows effective homogeneous heating of the reaction mixture and subsequent polycondensation reaction leading to the polymer formation. The optimum reaction time (irradiation time) was found in the range of 7-9 min. Below this time, the resulting polymers showed lower inherent viscosities and above this time the polymeric materials were degraded.

Polymer Characterization. The reaction conditions and inherent viscosities of poly(amide-imide)s **6a-f** are summarized in Table I. These polymers had inherent viscosities in a range of 0.33-0.52 dL/g and showed yellow color. The structures of these polymers were confirmed with those of poly(amide-imide)s designed by means of FT-IR spectroscopy and elemental analyses (Table II).

The representative FT-IR spectrum of poly(amide-imide)s **6a** is shown in Figure 1. The polymer shows absorption

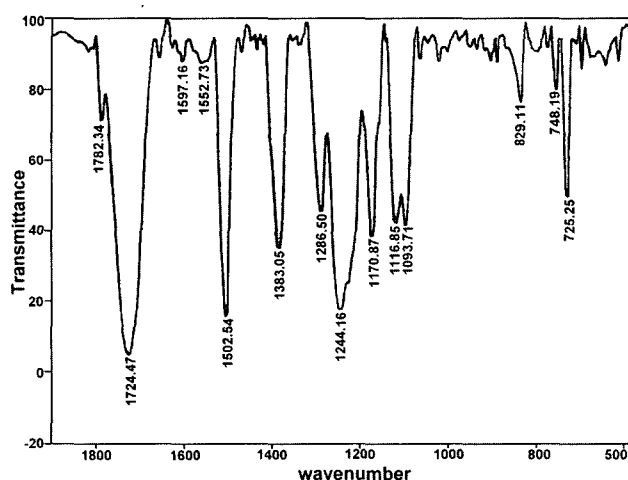
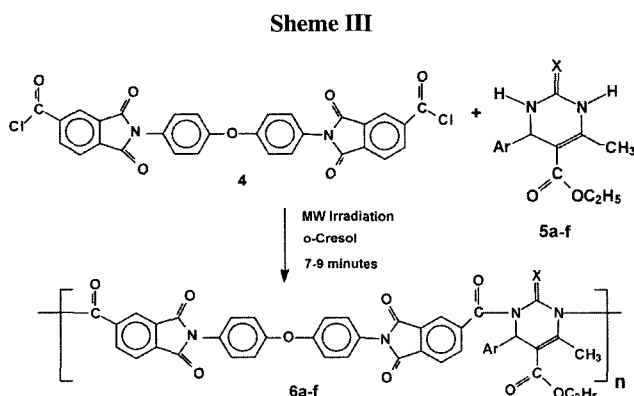


Figure 1. FT-IR Spectrum of polymer **6a**.

bands between 1780-1700 cm^{-1} due to imide, amide and ester carbonyl groups. Absorption bands around 1390-1370 and 730-710 cm^{-1} show the presence of imide heterocycle in this polymer. Absorption bands around 1200-1000 cm^{-1} which correspond to C-O stretching frequencies of ester. The other spectra show a similar pattern (See Table IV). The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table II).

The solubility behaviors of poly(amide-imide)s **6a-f** were investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in organic solvents such as DMF, DMAc, DMSO, NMP and THF at room temperature, but insoluble in solvents such as acetone, chloroform, methylene chloride, methanol, ethanol and water.

Thermal Properties. The thermal properties of two PAIs **6b** and **6f** were investigated by means of differential scanning calorimetry (DSC) as well as the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/$

Table I. Synthesis and Some Physical Properties of Poly(amide-imide)s **6a-f**

Polymer	Irradiation Time ^a (min)	Yield (%) ^b	η_{inh} (dL/g) ^c
6a	7	73	0.52
6b	8	70	0.45
6c	9	74	0.40
6d	8	91	0.33
6e	7.3	71	0.48
6f	9	81	0.50

^aTime of microwave irradiation. ^bPower of microwave irradiation is 900 W. ^cMeasured at a concentration of 0.5g/dL in DMF at 25 $^{\circ}\text{C}$.

Table II. Elemental Analysis of Poly(amide-imide)s **6a-f**

Polymer	Formula		C%	H%	N%
6a	$\text{C}_{44}\text{H}_{28}\text{N}_4\text{O}_{10}$	calcd	68.41	3.62	7.25
	$(772.44)_n$	found	67.7	4.0	6.9
6b	$\text{C}_{44}\text{H}_{28}\text{N}_4\text{O}_9\text{S}$	calcd	67.02	3.55	7.10
	$(788.44)_n$	found	66.8	4.1	6.5
6c	$\text{C}_{44}\text{H}_{27}\text{N}_4\text{O}_{10}\text{Cl}$	calcd	65.48	3.34	6.94
	$(806.94)_n$	found	66.1	3.9	6.0
6d	$\text{C}_{44}\text{H}_{27}\text{N}_4\text{O}_9\text{SCl}$	calcd	64.21	3.28	6.80
	$(822.94)_n$	found	65.0	4.0	5.9
6e	$\text{C}_{46}\text{H}_{32}\text{N}_4\text{O}_{12}$	calcd	66.36	3.84	6.72
	$(832.46)_n$	found	67.2	3.3	6.2
6f	$\text{C}_{46}\text{H}_{32}\text{N}_4\text{O}_{11}\text{S}$	calcd	65.11	3.77	6.60
	$(848.46)_n$	found	64.7	4.2	6.1

min and the thermal dates are summarized in Table III. All of these polymers show similar decomposition behavior (Figures 2, 3). Initial decomposition temperature, 5% and 10% weight loss (T_5 , T_{10}) and char yields at 600°C for poly(amide-imide)s **6b** and **6f** are summarized in Table III. These polymers exhibited good resistance to thermal

decomposition up to 295°C in nitrogen and began to decompose gradually above that temperature. The temperatures of 5% weight loss for all polymers were ranged from 290 to 310°C and the residual weights for these polymers at 600°C were ranged from 11.2 to 16.0% in nitrogen.

Table III. Thermal Behavior of Poly(amide-imide)s 6b,f

Polymer	T_g^a	T_5 (°C) ^b	T_{10} (°C) ^c	Char Yield ^d
6b	155	290-295	330-335	16.0
6f	165	310-315	355-355	11.2

^aGlass transition temperature. ^{b,c}Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂, respectively. ^dPercentage weight of material left after 600°C.

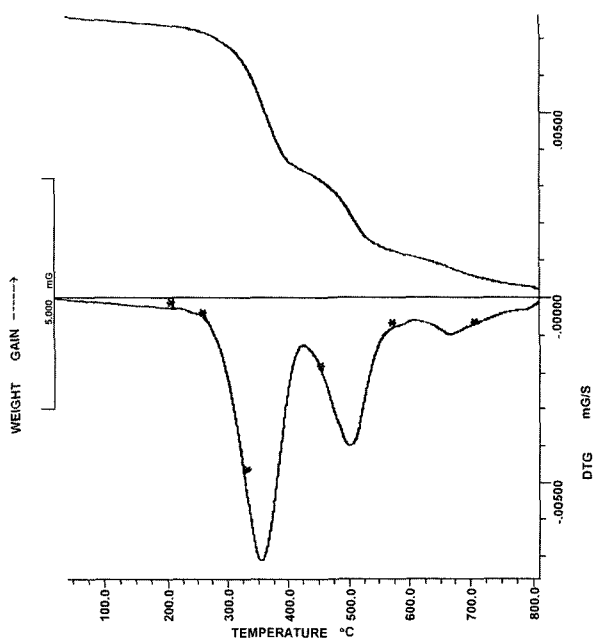


Figure 2. TGA and DTG thermogram of polymer **6b**.

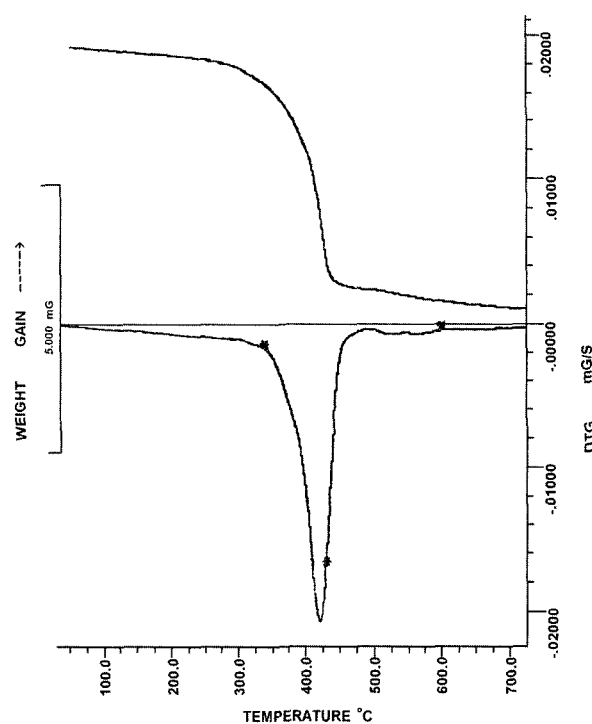


Figure 3. TGA and DTG thermogram of polymer **6f**.

Table IV. The FT-IR Spectra of PAIs 6a-f

Polymer	FT-IR Spectra
6a	1782 (m, sh), 1724 (s, br), 1502 (s), 1383 (s), 1286 (m), 1250-1220 (s, br), 1170 (s), 1116 (m), 1093 (m), 829 (w), 748 (w), 725 (m) cm ⁻¹
6b	1780 (m, sh), 1722 (s, br), 1622 (w), 1502 (s), 1482 (w), 1381 (m, br), 1284 (m), 1250-1220 (s, br), 1170 (s), 1106 (m), 1095 (m), 1058 (w), 842 (w), 750 (m), 725 (m) cm ⁻¹
6c	1780 (m, sh), 1724 (s, br), 1502 (s), 1381 (m), 1284 (m), 1245-1220 (s, br), 1170 (s), 1116 (m), 1100 (m), 1058 (w), 879 (w), 831 (w), 752 (m), 725 (m) cm ⁻¹
6d	1780 (m, sh), 1724 (s, br), 1595 (w), 1500 (s, br), 1381 (s), 1284 (s, sh), 1250-1220 (s, br), 1170 (s), 1114 (m), 1093 (s), 891 (w), 829 (w), 750 (m), 725 (m) cm ⁻¹
6e	1780 (m, sh), 1724 (s, br), 1502 (s, br), 1381 (m), 1286 (m), 1250-1220 (s, br), 1170 (s), 1114 (m), 1095 (m), 1058 (w), 829 (w), 750 (w), 725 (m) cm ⁻¹
6f	1780 (m, sh), 1722 (s, br), 1649 (w), 1502 (s), 1381 (m), 1284 (m), 1250-1220 (s, br), 1170 (s), 1116 (m), 1093 (m), 1058 (w), 827 (w), 750 (m), 723 (m) cm ⁻¹

imide)s **6a-f** could be synthesized by microwave assisted polycondensation reaction using the monomer **4** with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds **5a-f**. These new poly(amide-imide)s were soluble in various organic solvents and have good thermal stability. The above results demonstrate that the microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. We are currently studying the synthesis of novel monomers, polymers, and the modification of polymers by using this method.

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