

Microwave Heating in Conjunction with Ionic Liquid as a Novel Method for the Fast Synthesis of Optically Active Poly(amide-imide)s Derived from *N,N'*-(4,4'-Hexafluoroisopropylidenedipthaloyl)-bis-*L*-methionine and Various Aromatic Diamines

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ABSTRACT

Ionic liquids (ILs) are a new class of solvents which have interesting properties such as nonvolatility, high ionic concentration, good thermal stability, nonflammability and can dissolve most of organic as well as inorganic materials. Recently ILs are attracting more attention due to their significant role in controlling the reaction as a catalyst. It is important that ILs are the chemicals that can be applied as solvents and catalysts in green chemistry processes. In this investigation high molecular weight and optically active poly(amide-imide)s (PAIs) have been synthesized and their properties such as optical activity, solubility, thermal stability were studied. Polymers were synthesized by direct polymerization of *N,N'*-(4,4'-hexafluoroisopropylidenedipthaloyl)-bis-*L*-methionine and various aromatic diamines in the presence of triphenyl phosphite by a new microwave-assisted ionic liquid (MAIL) method. The compounds obtained were characterized by elemental C, H and N analysis, solubility, FTIR, ¹H NMR. Thermogravimetric curves were also recorded. All data agree with the proposed structures.

Key Words:

poly(amide-imide)s;
microwave-assisted;
optically active polymers;
direct polycondensation;
ionic liquid (IL).

INTRODUCTION

Many chemical processes involve volatile organic solvents that evaporate into the atmosphere with detrimental effects on the environment and human health. As the introduction of cleaner technologies has become a major concern throughout

both industry and academy, the search for alternatives to the damaging volatile solvents has become a high priority. Room temperature ionic liquids (RTILs) have aroused increasing interest worldwide due to their high fluidity, low melting tem-

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perature and extended temperature range in the liquid state, air and water stability, low toxicity, nonflammability, high ionic conductivity, ability to dissolve materials, and importantly no measurable vapour pressure [1-4]. Therefore, negative environmental and safety problems arising from the use of volatile organic solvents can be avoided by using RTILs. Because of the above reasons, RTILs are actively being explored as possible "green" solvents [5] to substitute conventional volatile organic solvents in a variety of processes, including industrially important chemical processes [6-10]. They also offer fascinating possibilities for fundamental studies of their effects on chemical reactions and synthetic processes [1-3,11].

The application of microwave heating in synthetic chemistry is a fast-growing area of research [12-13]. Since the first reports of microwave-assisted synthesis in 1986 [14-15], microwave heating has been accepted as a promising method for rapid volumetric heating, which results in higher reaction rates and selectivities, reduction in reaction times often by orders of magnitude, and increasing yields of products compared to conventional heating methods. As a result, this has opened up the possibility of realizing new reactions in a very short time. From the perspective of microwave chemistry, one of the key important advantages of RTILs is the presence of large organic positive ions with a high polarizability. Therefore, RTILs are very good media for absorbing microwaves, thus leading to a very high heating rate. There has been a recent report [16] on the use of ionic liquids as aids for microwave heating of nonpolar solvents, thereby allowing them to be used as media for microwave-assisted chemistry. The addition of a small quantity of an ionic liquid to a nonpolar solvent can greatly increase the rate and yield of reactions. However, the application of microwave chemistry to materials synthesis in conjunction with ionic liquids has hardly been exploited despite these advantages. By combining the advantages of both RTILs and microwave heating, a new microwave-assisted ionic liquid (MAIL) method for the fast controlled synthesis have been developed [17-21]. Recently, we have synthesized optically active polymers by different methods [22-24]. Herein we demonstrate that the MAIL method is a fast, highly efficient, and environmentally friendly green route for the production of optically active PAIs derived from *N,N'*-(4,4'-hexafluoroisopropylidenediph-

thaloyl)-bis-*L*-methionine and various aromatic diamines in the presence of triphenyl phosphite.

EXPERIMENTAL

Materials

4,4'-Diaminodiphenylmethane (**5b**) and 4,4'-diaminobiphenyl (**5f**) were purified by recrystallization from water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), were purified by sublimation. *N*-(Trimethylsilyl)-imidazol and all of the alkyl halides were purchased from Merck Chemical Co. (Germany). The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany), and were used without further purification.

Apparatus

The apparatus used for the polycondensation was a Samsung microwave oven (2450MHz, 900W). All of the polymerization reactions were performed in a hood with strong ventilation. Proton nuclear magnetic resonance ¹H NMR (500 MHz) spectra were recorded on a Bruker, Avance 500 instrument (Bruker, Rheinstetten, Germany). Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on Jasco-680 (Jasco-Japan) spectrophotometer. Spectra of solids were obtained with KBr pellets. Vibration bands were reported in wavenumber (cm⁻¹). The band intensities are classified as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske routine viscometer (Cannon-Mainz, Germany). The specific rotations were measured with a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer TGA 7 (Perkin Elmer, Jugeshein, Germany) in nitrogen atmosphere at a rate of 20°C/min. Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I.R. Iran.

Synthesis of Monomer

N,N'-(4,4'-Hexafluoroisopropylidenediphthaloyl)-bis-

L-methionine

One gram (2.2 mmol) of 4,4'-hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride) (**1**), 0.82 g (5.5 mmol) of L-methionine (**2**), 30 mL of acetic acid and a stirring bar were placed into a 50 mL round-bottomed flask. The mixture was stirred at room temperature for 3 h and then was refluxed for 8 h. The solvent was removed under reduced pressure and 5 mL of cold concentrated HCl was added to the residue. A white precipitate was formed and washed with cold water, and dried under reduced pressure to give 1.47 g (93.2% of compound **4**). mp: 136-138°C, $[\alpha] = 82.2 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$ (0.050 g in 10 mL DMF); FTIR (KBr): 2919 (m, br), 1778 (m), 1717 (s), 1624 (m), 1436 (w), 1384 (s), 1257 (s), 1211 (m), 1143 (m), 1093 (m), 964 (m), 850 (m), 630 (w) cm^{-1} . $^1\text{H NMR}$ (DMSO- d_6 , 500 MHz): $\delta = 2.00$ (s, 6H, $\text{CH}_3\text{-S}$), 2.40 (m, 4H, CH_2), 2.5 (m, 4H, $\text{CH}_2\text{-S}$), 4.96-4.98 (m, 2H, CH-N), 7.54-7.60 (s, 2H, Ar-H), 7.89-7.90 (d, 2H, $J = 5.0 \text{ Hz}$, Ar-H), 8.07-8.09 (d, 2H, $J = 10.0 \text{ Hz}$, Ar-H), 13.25 (s, br, 2H, COOH) ppm.

$\text{C}_{29}\text{H}_{24}\text{F}_6\text{N}_2\text{O}_8\text{S}_2$ (706.55): Calcd C, 49.29; H, 3.42; N, 3.96. Found: C, 49.21; H, 3.43; N, 4.11.

Typical Experimental Procedure for the Preparation of Symmetrical IL

N-Trimethylsilylimidazole (4.2 mL, 28.6 mmol), *n*-propyl bromide (8.00 mL, 85.8 mmol) and toluene (30.0 mL) were refluxed for 10 h and the crystalline product was isolated by filtration. 1,3-Dipropylimidazolium bromide was dissolved in dry MeCN and admixtures were removed by means of extraction with hexane. After the removal of MeCN, the product was dried in vacuo for 5 h; yield: 6.28 g (89.3%), $^1\text{H NMR}$ (acetone- d_6): δ , 0.89 (t, 6 H, CH_3 , $J_{(\text{HH})} = 7.34 \text{ Hz}$), 1.95 (sext, 4 H, $-\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{(\text{HH})} = 7.25 \text{ Hz}$), 4.49 (t, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_3$, $J_{(\text{HH})} = 7.20 \text{ Hz}$), 8.15 (s, 2 H, $\text{H}^{4,5}$ (Im)), 10.27 (t, 1 H, H^2 (Im)) ppm [25].

The other ILs 8-16 were prepared with similar procedure.

Polymerization

The PAIs were prepared by the following general procedure (using polymer **6a** as an example, 0.10 g (0.14 mmol) of diacid **4** and 0.034 g (0.14 mmol) of diamine **5a** were dissolved in 0.15 g of IL under heating, then was added 0.15 mL (0.56 mmol) of triphenyl phosphite

(TPP) into a porcelain dish. The dish was covered with a watch glass and subjected to microwave irradiation at power level of 540 w for the time of 50+30 s. The resulting product was isolated by adding methanol and triturating, following by filtration and was dried at 80°C for 10 h under vacuum to leave 0.12 g (94.2%) of solid **6a**; $^1\text{H NMR}$ (DMSO- d_6 , 500 MHz): $\delta = 2.00$ (s, 6H, $\text{CH}_3\text{-S}$), 2.20 (m, 4H, CH_2), 2.40 (m, 4H, $\text{CH}_2\text{-S}$), 5.0 (m, 2H, CH-N), 7.77 (s, 2H, Ar-H), 7.90 (d, 2H, Ar-H), 8.07-8.09 (d, 2H, Ar-H), 10.0 (s, 2H, N-H) ppm.

RESULTS AND DISCUSSION

Monomer Synthesis

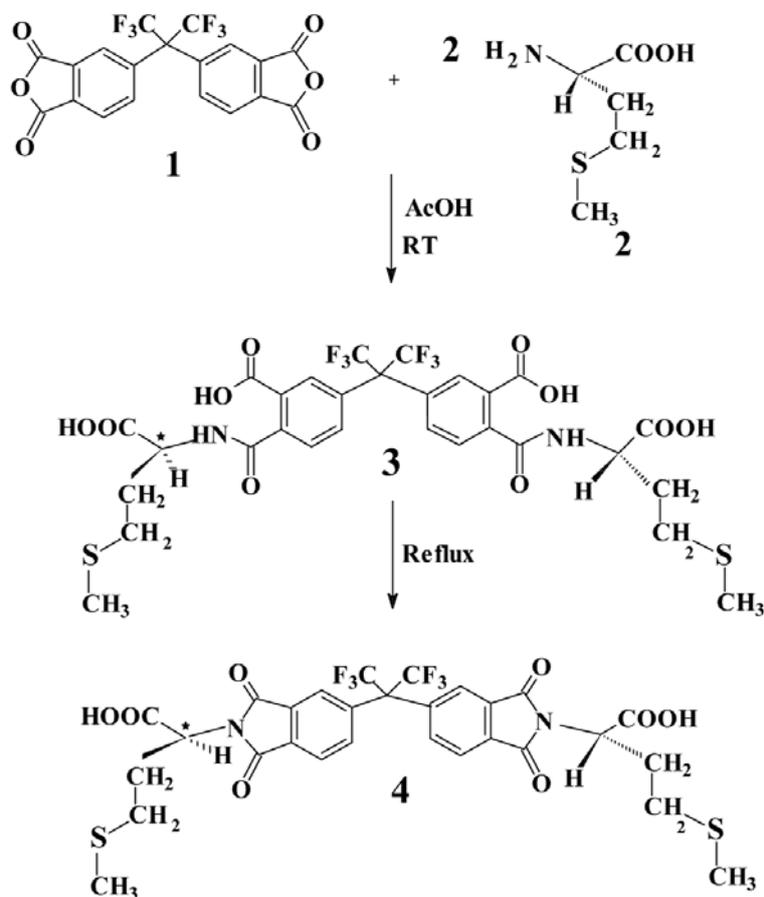
The diacid **4** was synthesized by the condensation of dianhydride **1** with two moles of L-methionine (**2**). The intermediate amic acid was not isolated and ring closure for the formation of the imide ring was performed under reflux conditions (Scheme I).

The chemical structure and purity of the compounds **4** were detected using elemental analysis, FTIR and $^1\text{H NMR}$ and $^{19}\text{F NMR}$ spectroscopic techniques. The $^{19}\text{F NMR}$ spectrum showed a single peak at -63.32 ppm and confirms the presence of F atoms and only one type of it in the new monomer **4**.

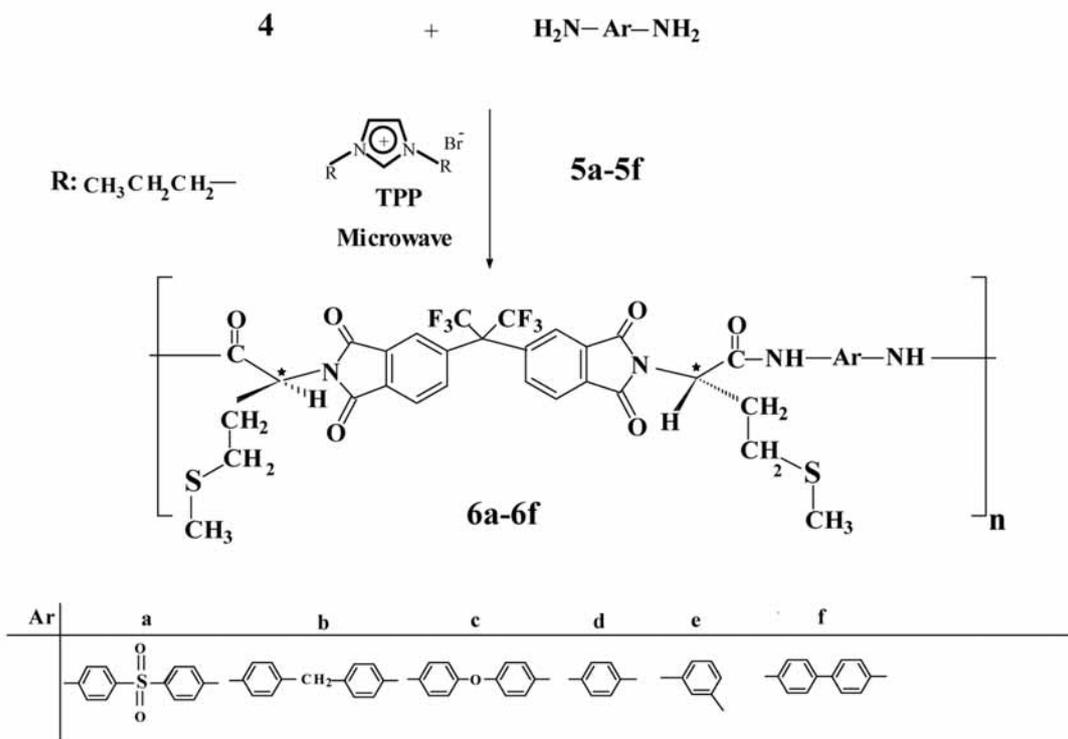
Polymer Synthesis

ILs bearing different alkyl groups and anions have been synthesized (IL 7-16) and their applications as a solvent and also a catalyst were examined for the direct polymerization reaction of monomer **4** with 4,4'-sulphonyldianiline. For these studies two different counter-ions such as Br^- , Cl^- were chosen. After optimizing all the conditions, several PAIs (**6a-6f**) were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer **4** with several different aromatic diamine (**5a-5f**) in an IL (**7**) media, which acting both as a solvent and a catalyst in conjunction with TPP under microwave irradiation (Scheme II). A reaction mechanism involving IL as a catalyst in conjunction with TPP has been reported [26].

Polycondensation was carried out by varying different ILs types, the amount of them, the duration of irradiation and power level of microwave instrument. It is interesting to mention that ILs which are highly polar media, efficiently absorb microwave energy and trans-



Scheme I. Synthesis of monomer 4.



Scheme II. Polycondensation reaction of monomer 4 with different aromatic diamines by method A.

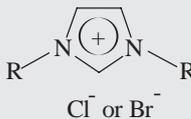
Table 1. Different conditions for the synthesis of PAI 6a under microwave irradiation.

Power level (%)	Time of reaction (s)	Amount of IL ^a g	Amount of cat. (mL)	Yield (%)	η_{inh} (dL/g) ^a
100	60	0.35	0.15	-	no polymer
100	50	0.35	0.15	-	-
100	30	0.35	0.15	-	-
100	20	0.35	0.15	-	-
90	60	0.35	0.15	-	-
90	50	0.35	0.15	-	-
90	30	0.35	0.15	-	-
90	20	0.35	0.15	-	-
80	60	0.35	0.15	-	-
80	50	0.35	0.15	-	-
80	30	0.35	0.15	-	-
80	20	0.35	0.15	-	-
70	60	0.35	0.15	-	-
70	50	0.35	0.15	-	-
70	30	0.35	0.15	-	-
70	20	0.35	0.15	-	-
60	60	0.35	0.15	-	-
60	60	0.30	0.15	-	-
60	60	0.20	0.15	57	0.22
60	60	0.15	0.15	65	0.35
60	70	0.15	0.15	71	0.38
60	80	0.15	0.15	-	-
60	50 + 20	0.15	0.15	80	0.55
60	50 + 30	0.15	0.15	94	0.79
60	50 + 30	0.10	0.15	78	0.60
60	50 + 40	0.15	0.15	66	0.51
60	50 + 50	0.15	0.15	59	0.45
50	50 + 30	0.15	0.15	48	0.41

^aIL= 1,3-Di-n-propylimidazolium bromide; diacid = 0.14 mmol; diamine = 0.14 mmol.

fer it to heat. All of these parameters had critical effect on the polymer chain growth (Tables 1 and 2). When the amount of IL was high the resulting starting materials turned to dark colour and burned. Even when the

Table 2. Influence of the reaction medium on the inherent viscosities, yield and rotation of optically active PAI 6a.

					
Code	R	Yield	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
7	CH ₃ -CH ₂ -CH ₂ - (Br-)	94.3	0.78	-55.1	-62.1
8	CH ₃ -CH-CH ₃ (Br-)	90.1	0.62	-44.1	-56.2
9	CH ₂ =CH-CH ₂ - (Br-)	86.2	0.70	-55.7	-60.0
10	CH ₂ =CH-CH ₂ - (Cl-)	88.1	0.68	-56.1	-59.2
11	CH ₃ -(CH ₂) ₃ -CH ₂ - (Br-)	95.2	0.69	-45.3	-50.2
12	CH ₃ -(CH ₂) ₄ -CH ₂ - (Br-)	93.1	0.69	-54.3	-51.2
13	CH ₃ -(CH ₂) ₅ -CH ₂ - (Br-)	91.4	0.61	-52.1	-60.0
14	CH ₃ -(CH ₂) ₈ -CH ₂ - (Br-)	76.3	0.62	-61.3	-69.1
15	C ₆ H ₅ -CH ₂ - (Br-)	92.1	0.63	-46.1	-50.3
16	C ₆ H ₅ -CH ₂ - (Cl-)	90.3	0.75	-40.3	-44.2

Diacid = 0.14 mmol; diamine = 0.14 mmol; IL = 0.15 g; power level = 60 %

power level was lowered we did not obtain any polymeric materials and they burned. Therefore, the shorter period and lower microwave power level were quite necessary, otherwise too vigorous reaction would occur leading to the degradation of the reaction mixture.

The optimum conditions which were obtained have been applied for the preparation of PAIs and the results are demonstrated in Table 3.

Some physical properties of these novel optically active PAIs under optimum conditions are listed in Table 4. The inherent viscosities of the resulting poly-

Table 3. Optimum conditions for the preparation of PAI **6a**.

Power level (%)	
Suitable IL	
Amount of IL (g)	0.15
Power level (%)	60
Reaction time (s)	50 + 30

mers were in a range of 0.66-0.94 dL/g and the yields were 92-96%. All of the PAIs show optical rotations, therefore are optically active.

In order to study the effect of ILs on the polymerization process, two methods of polymerization were used for preparation of the PAIs from related monomers. These are so called direct MAIL (method A) and microwave-assisted indirect (method B). As shown in Scheme II, by method A, synthesis and separation of diacid chloride is not necessary, and the reaction proceeds as one pot reaction starting from free dicarboxylic acid. On the other hand in method A we

Table 4. Some physical properties of PAIs **6a-6f** synthesized under the optimum conditions.

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$	$[\alpha]_{Hg}^{25}$
5a	6a	94.2	0.78	-42.3	51.3
5b	6b	96.3	0.72	-46.3	-72.3
5c	6c	93.2	0.84	-54.2	-66.3
5d	6d	94.3	0.66	-60.3	-64.3
5e	6e	96.1	0.90	-55.6	-61.2
5f	6f	92.1	0.94	-70.3	-82.3

$[\alpha]_D^{25}$ = Specific Rotation = deg dm⁻¹ g⁻¹ cm³.

used IL as a solvent, and a catalyst. Replacement of a volatile organic solvent such as *o*-cresol in polymerization with non-volatile solvent ILs will reduce losses through evaporation and it is important that ILs are the chemicals that can be applied as solvents and catalysts at the same time in green chemistry process. The possibility of recovery and reuse of IL/catalyst system and

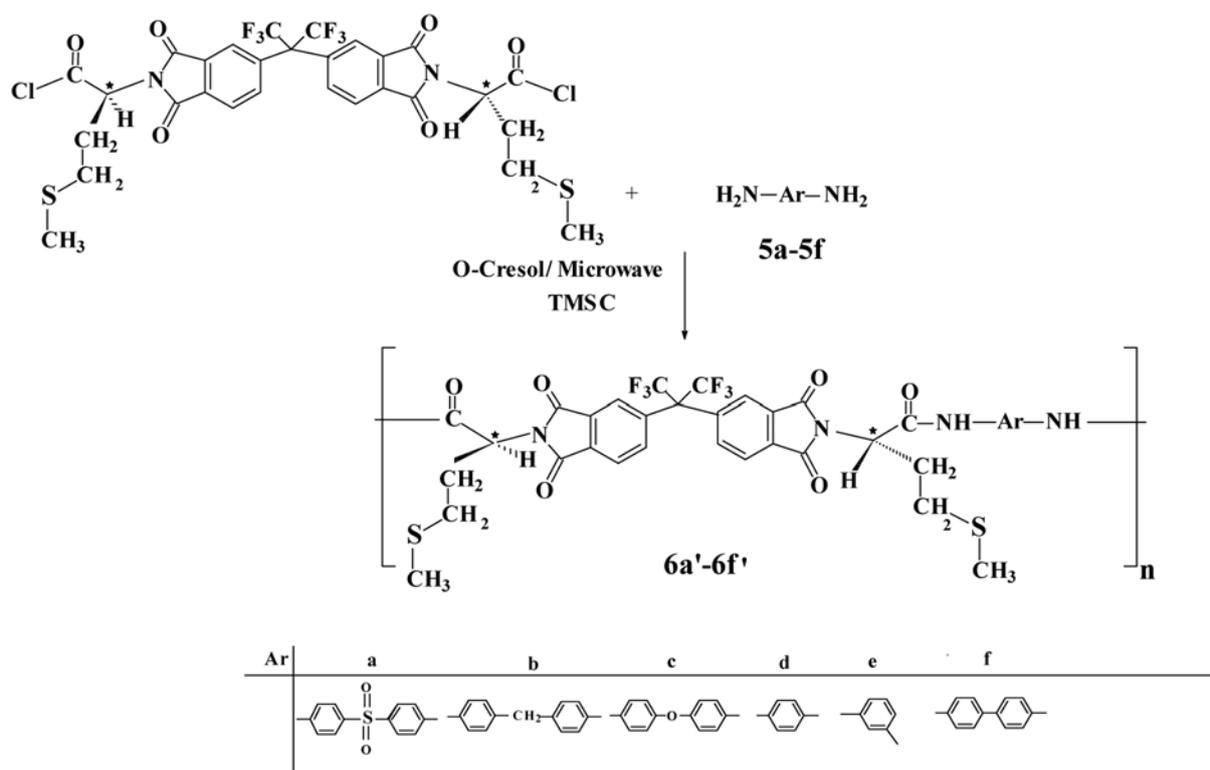
**Scheme III.** Polycondensation reaction of related diacid with different aromatic diamines by method B.

Table 5. Comparison of some physical properties data referring to the PAIs 6a-6f synthesized by methods A and B, under the optimum conditions.

Diamine	Polymer				
	Polymer	Yield (%) ^a	η_{inh} (dL/g) ^a	Yield (%) ^b	η_{inh} (dL/g) ^b
5a	6a	95.2	0.78	93.2	0.45
5b	6b	96.3	0.72	88.3	0.35
5c	6c	93.2	0.84	83.2	0.28
5d	6d	94.3	0.66	92.3	0.36
5e	6e	96.1	0.90	86.3	0.32
5f	6f	92.1	0.94	85.1	0.33

(^a) Method A: Direct polycondensation of imide containing diacid and aromatic diamines using IL and TPP in the optimum conditions under microwave irradiation; (^b) Method B: Solution polycondensation of diacid chloride and aromatic diamines using trimethylsilyl chloride (TMSC) and *o*-cresol as a solvent under microwave irradiation.

ability to dissolve monomers are other advantages of using ILs system in method A.

However, in method B, which is a classic procedure, diacid should be introduced as diacid chloride in

the polymerization vessel [27]. On the other hand, method B was carried out by *o*-cresol as a volatile organic solvent (Scheme III).

In Table 5, products yields and inherent viscosities of the resulting polymers prepared by both methods are compared. The yields and inherent viscosities are higher for method A than method B.

FTIR and ¹H NMR Data

FTIR spectra of all polymers show the characteristic absorption peaks for the imide ring at 1780 and 1718 cm⁻¹ due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared ca. 3345 cm⁻¹ (hydrogen bonds) and 1455-1511 cm⁻¹ (amide II bonds). All of them exhibited strong absorptions at 1381 cm⁻¹ and 750 cm⁻¹ that show the presence of the imide heterocycle ring in these polymers. The pattern of ¹H NMR spectra is similar to those of monomer diacid chloride and corresponding diamine. The ¹⁹F NMR spectrum of PAI6aI shows only one peak at -63.25 ppm which also confirms the presence of F atom and only one type of it in the resulting polymer backbone. Elemental analysis data of the resulting polymers are listed in Table 6.

Most of the polymers are soluble in aprotic polar solvents such as DMF, *N,N*-DMAC, dimethyl sulphox-

Table 6. Elemental analysis of PAIs 6'a-6'f.

Polymer	Formula		Elemental analysis (%)		
			C	H	N
6a	(C ₄₁ H ₃₂ N ₄ O ₈ S ₃ F ₆) _n (918.8) _n	Calcd	53.59	3.51	6.09
		Found	53.61	3.50	6.26
6b	(C ₄₂ H ₃₄ N ₄ O ₆ S ₂ F ₆) _n (869.8) _n	Calcd	58.06	3.94	6.44
		Found	58.11	3.98	6.63
6c	(C ₄₁ H ₃₂ N ₄ O ₇ S ₂ F ₆) _n (870.7) _n	Calcd	56.55	3.70	6.43
		Found	56.61	3.71	6.56
6d	(C ₃₅ H ₂₈ N ₄ O ₆ S ₂ F ₆) _n (778.6) _n	Calcd	53.98	3.62	7.19
		Found	53.91	3.65	7.31
6e	(C ₃₅ H ₂₈ N ₄ O ₆ S ₂ F ₆) _n (778.68) _n	Calcd	53.98	3.62	7.19
		Found	53.90	3.63	7.30
6f	(C ₄₁ H ₃₂ N ₄ O ₆ S ₂ F ₆) _n (854.78) _n	Calcd	57.61	3.77	6.55
		Found	57.69	3.79	6.69

$[\alpha]_D^{20}$ = Specific rotation = deg dm⁻¹ g⁻¹ cm³.

Table 7. Thermal properties of PAIs **6a** and **6b**.

Polymer	T5 (°C) ^a	T10 (°C) ^b	Char yield (%) ^c
6a	511	637	81
6b	452	540	75

^(a) Temperature at which 5% weight loss was recorded by TGA at heating rate of 20°C/min in N₂; ^(b) temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min in N₂; ^(c) percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in N₂.

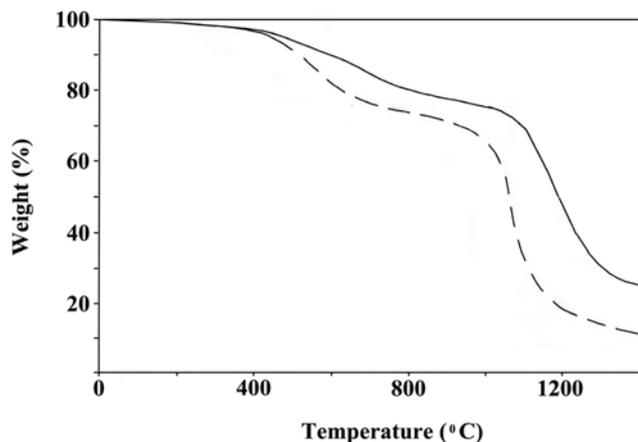


Figure 1. TGA of PAI **6a** (—) and PAI **6b** (-----) at a heating rate of 20°C/min under a nitrogen atmosphere.

ide (DMSO), NMP. They are insoluble in chloroform, acetonitril, cyclohexane and water.

Thermal Properties

Thermal gravimetric analysis (TGA) was used in order to investigate the thermal properties of the PAIs. Some thermal behaviour data for PAI **6a** and **6b** are listed in Table 7. These results show excellent thermal stabilities of the polymers. The temperature at which the decomposition begins is never under 378°C. The highest thermal stability was shown by PAIs **6aI**. This behaviour could be a consequence of the sulphone moieties presence in the main chain of polymer. Typical TGA curves of representative polymers are shown in Figure 1.

CONCLUSION

For the first time high-molecular-weight and optically active PAIs have been synthesized by direct polycondensation reactions in various ILs which act as reaction

media and a catalyst under microwave irradiation. The nature and amount of the ILs have highly influence on the polymerization process and the molecular weights of the polymers. By varying the structures of cations and anions of the ILs, it is possible to tailor ILs as active solvents for polycondensation reactions. In summary, we have developed a facile methodology for the synthesis of optically active polymers in ILs by using microwave irradiation. The green solvent is harmless, economical, and environmentally friendly. The catalyst system was very easy to separate from the reaction product, so it can be used repeatedly. The microwave irradiation is very favourable for us. These ILs catalysts can be effectively recycled, thus rendering this expeditious protection protocol more efficient and ecofriendly.

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