

Microwave-Assisted and Classical Heating Polycondensation Reaction of bis(*p*-Amido benzoic acid)-*N*-trimellitylimido-*L*-leucine with Diisocyanates as a New Method for Preparation of Optically Active Poly(amide imide)s

Shadpour Mallakpour,* Fatemeh Rafiemanzelat

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156, I.R. Iran

Received 8 October 2003; accepted 8 March 2004

DOI 10.1002/app.20603

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new class of optically active poly(amide imide)s were synthesized via direct polycondensation reaction of diisocyanates with a chiral diacid monomer. The step-growth polymerization reactions of monomer bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL) (5) as a diacid monomer with 4,4'-methylene bis(4-phenylisocyanate) (MDI) (6) was performed under microwave irradiation, solution polymerization under gradual heating and reflux condition in the presence of pyridine (Py), dibutyltin dilurate (DBTDL), and triethylamine (TEA) as a catalyst and without a catalyst, respectively. The optimized polymerization conditions according to solvent and catalyst for each method were performed with tolylene-2,4-diisocyanate (TDI) (7), hexamethylene diisocyanate (HDI) (8), and isophorone diisocyanate (IPDI) (9) to produce optically active poly-

(amide imide)s by the diisocyanate route. The resulting polymers have inherent viscosities in the range of 0.09–1.10 dL/g. These polymers are optically active, thermally stable, and soluble in amide type solvents. All of the above polymers were fully characterized by IR spectroscopy, ¹H NMR spectroscopy, elemental analyses, specific rotation, and thermal analyses methods. Some structural characterization and physical properties of this new optically active poly(amide imide)s are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1647–1659, 2004

Key words: thermogravimetric analysis (TGA); microwave; polycondensation; diisocyanates; poly(amide imide)s; optically active polymers

INTRODUCTION

Recently, polymers with optically active properties have found interesting applications, including chiral phases for enantiomeric separations in chromatography methods, chiral media for asymmetric synthesis,^{1–5} chiral liquid crystals in ferroelectrics, and nonlinear optical devices.^{6–9} As such, the synthesis of optically active polymers is a topic that has sparked more attention. Especially, the synthesis of polymers containing amino acids has been a subject of much interest, because a high degree of amino acid functionality can lead to polymers with increased solubility and the ability to form secondary structures.^{10,11} Possible applications of amino acid-based polymers include drug delivery agents, chiral recognition station-

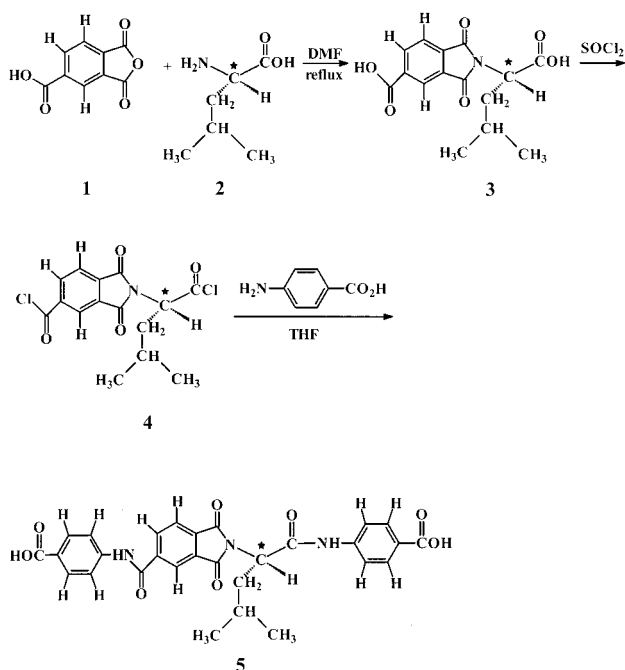
ary phases, asymmetric catalysts, metal ion absorbents, and biomaterials.^{11–13} In the last new decade, we synthesized optically active polymers by different methods,^{14–22} such as the modification of polybutadiene with an optically active substituted urazole group,¹⁴ Diels-Alder ene reaction,^{15,16} and the reaction of an optically active monomer with several diamines or diols via solution polymerization.^{17–22} In these polycondensation reactions, we used amino acids as chiral inducing agents. These naturally occurring compounds, and so synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

Poly(amide imide)s (PAI)s are well known as a class of polymers with good compromise between processability and performance.^{23–31} Conventionally, PAIs based on trimellitic anhydride (TMA) are prepared in several ways,^{32–35} including polycondensation of TMA or TMA-derived imide ring-containing dicarboxylic acids with diisocyanates.^{36,37} In fact, most preparative methods known for creating amide linkage are based on polycondensation reactions between diamines and diacyl chlorides or direct polycondensation reactions between diamines and diacids, but little work has been reported on

Correspondence to: S. Mallakpour (mallak@cc.iut.ac.ir).

*Previous name: Shadpour E. Mallakpour.

Contact grant sponsors: the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, and Center of Excellency in Chemistry Research (IUT).



Scheme 1 Preparation of monomer (5).

the synthesis of polyamides, copolyamides, or polyimides based on direct polycondensation reactions between diacids and diisocyanates.^{38–47}

Isocyanates are highly reactive compounds that have been widely used for the synthesis of a large variety of organic derivatives. The application of diisocyanates in the field of polymer chemistry has led to the successful preparation of many novel polymers with versatile properties.⁴⁸

Moreover, in recent years, organic reactions assisted by microwave irradiation have gained special attention. The reactions are very fast, and completed within 10 min.^{49–53} Recently, we have used microwave irradiation for the synthesis of organic compounds as well as macromolecules.^{21,22,54–58}

In this article for the first time we wish to report the microwave assisted synthesis of optically active poly-(amide imide)s containing TMA and *L*-leucine moieties from direct polycondensation of aromatic diacid (5) and diisocyanates upon the isocyanate route, and compare this method with conventional solution polymerization reactions. In this work we set out to investigate the effect of different reaction conditions such as solvent effect, reaction time, reaction temperature, and reaction methods (microwave irradiation and classical heating) on the properties of polymers including solubility, viscosity, and thermal behaviors.

EXPERIMENTAL

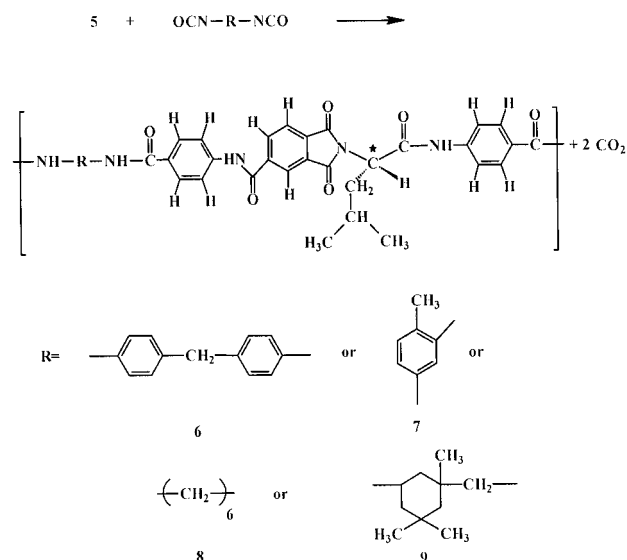
Materials and equipments

Reagents were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Riedel-deHaen AG

(Seelze, Germany). *N,N*-Dimethylacetamide (DMAc), dimethylsulfoxid (DMSO), *N,N*-dimethylformamide (DMF), pyridine (Py), and triethylamine (TEA) were dried over BaO and then were distilled under reduced pressure. MDI was used as received. Bis(*p*-amidobenzoic acid)-*N*-trimellitylimido-*L*-leucine BPABTL (5) was prepared according to the reported procedure.⁵⁹ The yield of the diacid (5) was 98%, m.p. > 275°C (dec), and $[\alpha]_D^{25}$: +17.6 [0.0520 g in 10 mL of DMF].

Proton nuclear magnetic resonance ¹H NMR (500 MHz) spectra were recorded on a Bruker (Rheinstetten, Germany), Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). FTIR spectra were recorded on a Nicolet impact 400_D IR spectrophotometer (London, England). 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 a standard procedure using a Cannon-Fensck Routine Viscometer (Mainz, Germany). Specific rotations were measured by a Perkin-Elmer-241 Polarimeter (Jugesheim, Germany).

The microwave apparatus used for the polycondensation was a Samsung (South Korea) domestic microwave oven (2450 MHz, 900 W) without any modification, but all of the polymerization reactions were carried out in a hood with strong ventilation. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a TGA Perkin-Elmer (Jugesheim, Germany) 4 Thermal analyzer under air atmosphere, and the first run of Differential Scanning Calorimetry (DSC) data were recorded on a



Scheme 2 Polycondensation reactions of monomer (5) with diisocyanates.

TABLE I
Reaction Conditions for the Polymerization of Monomer BPABTL (5) with MDI (6)
by Different Methods and Some Physical Properties of PAI-PAI₁₂

Polymer	Method ^a	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	[α] _D ²⁵
PAI ₁	I	NMP ^b	Py ^c	A	MeOH/Water	60	0.115 ^f	-0.031 ^f
PAI ₂	I	NMP	DBTDL ^d	A	MeOH/Water	60	0.194 ^f	-0.180 ^f
PAI ₃	I	NMP	TEA ^c	A	MeOH/Water	59	0.098 ^f	-0.190 ^f
PAI ₄	I	NMP	NO Cat.	A	MeOH/Water	60	0.210 ^f	-0.000 ^f
PAI ₅	II	DMAc	Py	1.25 ^h	MeOH	49	1.105 ^g	-1.830 ^g
PAI ₆				1.25 ^h		90	0.290 ^f	-1.361 ^f
PAI _{6'}	II	DMAc	DBTDL	2.5 ^h	MeOH/Water	80	0.200 ^f	—
PAI ₇	II	DMAc	TEA	1.25 ^h	MeOH	71	0.410 ^f	-0.670 ^f
PAI ₈	II	DMAc	NO Cat.	1.67 ^h	MeOH	70	0.290 ^f	-0.930 ^f
PAI ₉	III	NMP	Py	3 ^h	MeOH/Water	95	0.410 ^f	-0.795 ^f
PAI ₁₀				6 ^b		77	0.360 ^f	-0.398 ^f
PAI _{10'}	III	NMP	DBTDL	3 ^h	MeOH/Water	80	0.301 ^f	—
PAI ₁₁	III	NMP	TEA	6 ^h	MeOH/Water	91	0.331 ^f	-0.196 ^f
PAI ₁₂	III	NMP	NO Cat	6 ^h	MeOH/Water	97	0.197 ^f	-0.391 ^f

^a Method I: Graduate heating at different temperature, Method II: Refluxing, Method III: Irradiating by a domestic microwave oven at 100% of its power.

^b *N*-methyl pyrrolidone.

^c Pyridine,

^d dibutyltin dilaurate,

^e triethylamine.

^f Measured at a concentration of 0.5 g/dL in DMF containing 2% W/W LiCl at 25°C.

^g Measured at a concentration of 0.2 g/dL in DMF containing 2% W/W LiCl (soluble fraction) at 25°C.

^h Minute. A: 2 h 0°C, 2 h RT, 2 h 60°C, 2 h 80–90°C, 0.5 h 100°C.

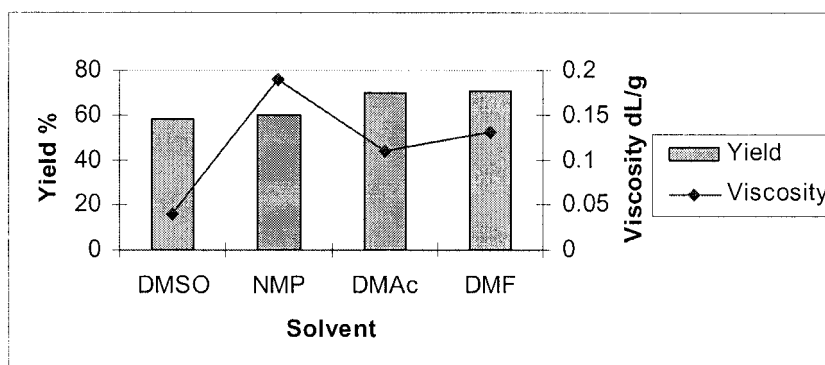
Perkin-Elmer (Jugesheim, Germany) DSC 7-TAC 7 DX Thermal Analyzer under air atmosphere by the Research Institute of Petroleum Industry, Tehran, I.R. Iran. Elemental analyses were performed by Malek Ashter University, Tehran, I.R. Iran.

Polymerization of BPABTL (5) with MDI (6)

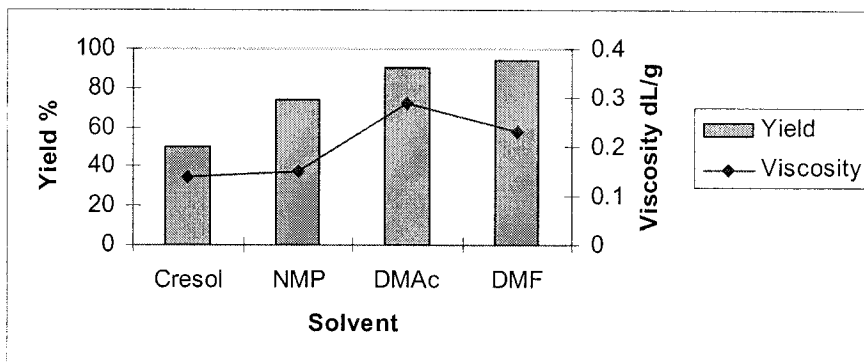
Method I

In a 25-mL round-bottom flask a solution of BPABTL (5) (0.1064 g, 1.96×10^{-4} mol) in 0.175 mL of 1-methyl-2-pyrrolidone (NMP) was added to a solution of MDI

(6) (0.0490 g, 1.96×10^{-4} mol) and DBTDL (0.0176 g, 2.78×10^{-5} mol) in 0.175 mL of dry NMP. The solution was stirred for 2 h at 0°C, 2 h at room temperature (RT), 2 h at 60°C, then it was heated gradually from 60 to 90°C for 4 h and finally for 0.5 h at 100°C. During of this period 0.200 mL of NMP was added. The reaction mixture was poured into 30 mL of methanol/distilled water mixture (50 : 50) to isolate the polymer. The solid was filtered off, dried to give 0.0828 g (60%) of yellow PAI₂. This polymerization was also repeated using Py and TEA as catalysts, and without any catalyst, respectively.



Curve 1 The effect of solvent on the viscosity dL/g and yield % of the PAIs-based MDI in the presence of DBTDL as a catalyst for method I.



Curve 2 The effect of solvent on the viscosity dL/g and yield % of the PAIs-based MDI in the presence of DBTDL as a catalyst for method II.

Method II

The above polymerization was repeated, but the reaction mixture was refluxed in DMAc in the presence of Py, DBTDL, or TEA as a catalyst and without any catalyst, respectively. As an example, preparation of PAI₅ is as follow: in a 5-mL round-bottom flask a solution of BPABTL (5) (0.0514 g, 9.46×10^{-5} mol) in 0.075 mL of dry DMAc and Py (0.015 mL, 1.89×10^{-4} mol) was stirred at RT for 0.5 h, then a solution of MDI (6) (0.0237 g, 9.47×10^{-5} mol) in 0.075 mL of dry DMAc was added. After stirring at RT for 2 h, the reaction mixture was heated by a heating mantle under an N₂ atmosphere. After 1.5 min a very viscose solution was formed that prevented the stirring by a magnetic bar. Then 10 mL of the methanol was added and under vigorous trituration the polymer was precipitated. The solid was filtered off and dried to give 0.0330 g (49%) of white PAI₅.

Method III

The PAIs were prepared by the following general procedure (with PAI₉ as an example): into a porcelain dish was placed BPABTL (5) (0.0902 g, 1.66×10^{-4} mol), and 0.200 mL of NMP was added. After the

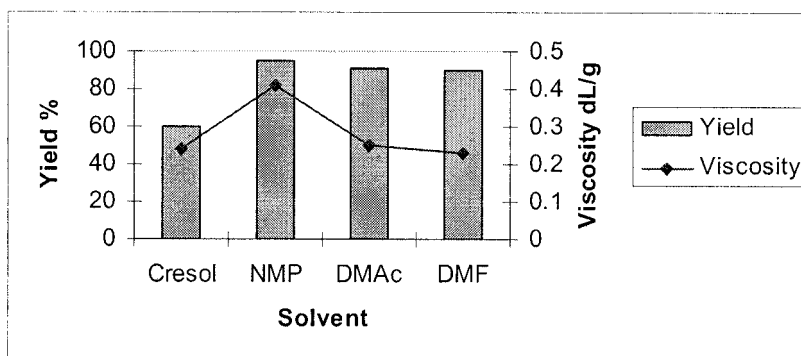
mixture was completely ground, Py (0.026 mL, 3.33×10^{-4} mol) was added, and the mixture was ground for 2 min; then a solution of MDI (6) (0.0417 g, 1.66×10^{-4} mol) in 0.110 mL of NMP was added, and the mixture was ground again for additional 3 min. The viscose reaction mixture was irradiated in the microwave oven for 3 min at 100% of its power. The resulting product was isolated by the addition of 20 mL of methanol/water mixture (60 : 40). It was then filtered and dried at 80°C for 10 h *in vacuo*; this yielded 0.1114 g (95%) of yellow PAI₉. The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven in NMP, using DBTDL or TEA as a catalyst and without a catalyst, respectively.

For each method the optimized reaction conditions according to reaction solvent, reaction time, and reaction catalysts were used for the polymerization of BPABTL (5) with other diisocyanates such as TDI, HDI, and IPDI.

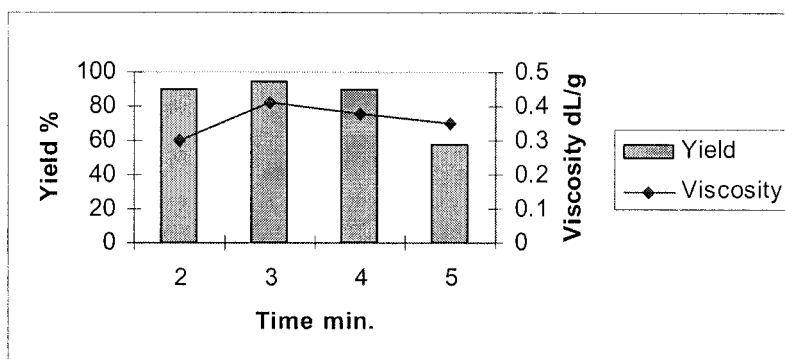
RESULTS AND DISCUSSION

Polymerization reactions

Monomer (5) was synthesized according to the reported procedure (Scheme 1).⁵⁹ The polymerization



Curve 3 The effect of solvent on the viscosity dL/g and yield % of the PAIs-based MDI in the presence of Py as a catalyst for method III.



Curve 4 The effect of the irradiation time on the viscosity dL/g and yield % of the PAIs-based MDI for method III in NMP in the presence of Py at 100% of power.

reactions of monomer (5) with diisocyanates were performed under microwave irradiation as well as conventional solution polymerization techniques in the presence of different catalysts and without a catalyst to afford PAI₁–PAI₃₀ (Scheme 2). The reaction of diisocyanates with diacids initially forms anhydrides linkages that are not stable under the reaction condition, and CO₂ evolved to produce amide linkages that were very stable.

The polymerization reactions of monomer (5) with MDI (6) were performed with three different methods in the presence of different catalysts and without a catalyst, respectively. The results of different reaction conditions are summarized in Table I. In method I the reaction mixture was heated gradually from 0°C up to 100°C in the presence of Py, DBTDL, TEA, and without a catalyst, respectively. The resulting polymers PAI₁–PAI₄ were obtained in moderate yields and low inherent viscosities (Table I). In method II, the reaction mixture was refluxed in DMAc. The resulting poly-

mers PAI₅–PAI₈ have moderate to high yields and high inherent viscosities, especially in the case of Py and TEA as catalysts (Table I). In method III, the polymerization reactions were performed in NMP under microwave irradiation in the presence of Py, DBTDL, or TEA and without a catalyst, respectively. The resulting polymers PAI₉–PAI₁₂ have high yields and moderate inherent viscosities, especially in the case of Py and DBTDL as catalysts (Table I). According to Table I, remarkable results for the polymerization of (5) with MDI (6) as far as viscosity and yield are taken into account, were obtained by method II in the presence of Py as well as TEA.

To optimize the effect of solvent on viscosities and yields of the polymers, the polymerization reactions were carried out in different solvents for each methods (Curves 1–3).

In the case of method I, solvents such as DMSO, NMP, DMAc, and DMF in the presence of DBTDL were tested. According to Curve 1 in DMAc and DMF,

TABLE II
Reaction Conditions for the Polymerization of Monomer BPABTL (5) with TDI (7) by Different Methods and Some Physical Properties of PAI₁₃–PAI₁₈

Polymer	Method ^a	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	[α] _D ²⁵
PAI ₁₃	I	NMP ^b	DBTDL ^d	A	Water	87	0.27 ^f	–0.000 ^f
PAI ₁₄	I	NMP	NO Cat	A	Water	96	0.177 ^f	–0.191 ^f
PAI ₁₅	II	DMAc	Py ^c	1.5 ^g	MeOH	70	0.131 ^f	–0.201 ^f
PAI ₁₆	II	DMAc	TEA ^c	10 ^g	MeOH/Water	62	0.110 ^f	–0.221 ^f
PAI ₁₇	III	NMP	Py	3 ^g	MeOH/Water	80	0.220 ^f	–0.210 ^f
PAI ₁₈	III	NMP	DBTDL	3 ^g	MeOH/Water	53	0.251 ^f	0.000 ^f

^a Method I: Graduate heating at different temperature, Method II: Refluxing, Method III: Irradiating by a domestic microwave oven at 100% of its power.

^b N-methyl pyrrolidone.

^c Pyridine,

^d dibutyltin dilaurate,

^e triethylamine.

^f Measured at a concentration of 0.5 g/dL in DMF containing 2% W/W LiCl at 25°C.

^g Minute. A: 2 h 0°C, 2 h RT, 2 h 60°C, 2 h 80–90°C, 0.5 h 100°C.

TABLE III
Reaction Conditions for the Polymerization of Monomer BPABTL (5) with HDI (8)
by Different Methods and Some Physical Properties of PAI₁₉–PAI₂₄

Polymer	Method ^a	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25}$
PAI ₁₉	I	NMP ^b	DBTDL ^d	A	MeOH/Water	97	0.416 ^f	-1.051 ^f
PAI ₂₀	I	NMP	NO Cat	A	MeOH/Water	76	0.419 ^f	-0.201 ^f
PAI ₂₁	II	DMAc	Py ^c	9 ⁱ	MeOH/Water	87.6	0.241 ^h	-0.360 ^h
PAI ₂₂	II	DMAc	TEA ^c	15 ⁱ	MeOH/Water	82	0.261 ^h	+0.410 ^h
PAI ₂₃	III	NMP	Py	3 ⁱ	MeOH/Water	80	0.201 ^f	-0.210 ^f
PAI ₂₄	III	NMP	DBTDL	3 ⁱ	MeOH/Water	70	0.610 ^g	-0.850 ^g

^a Method I: Graduate heating at different temperature, Method II: Refluxing, Method III: Irradiating by a domestic microwave oven at 100% of its power.

^b N-methyl pyrrolidone.

^c Pyridine,

^d dibutyltin dilaurate,

^e triethylamine.

^f Measured at a concentration of 0.5 g/dL in DMF containing 2% W:W LiCl at 25°C.

^g Measured at a concentration of 0.2 g/dL in DMF containing 2% W/W LiCl (soluble fraction) at 25°C.

^h Measured at a concentration of 0.5 g/dL in DMF containing 3% W/W LiCl at 25°C.

ⁱ Minute. A: 2 h 0°C, 2 h RT, 2 h 60°C, 2 h 80–90°C, 0.5 h 100°C.

TABLE IV
Reaction Conditions for the Polymerization of Monomer BPABTL (5) with IPDI (9)
by Different Methods and Some Physical Properties of PAI₂₅–PAI₃₀

Polymer	Method ^a	Solvent	Catalyst	Reaction time.	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25}$
PAI ₂₅	I	NMP ^b	DBTDL ^d	A	MeOH/Water	60	0.121 ^f	-0.401 ^f
PAI ₂₆	I	NMP	NO Cat	A	MeOH/Water	94	0.158 ^f	-0.201 ^f
PAI ₂₇	II	DMAc	Py ^c	20 ^h	Water	97	0.182 ^g	-0.197 ^g
PAI ₂₈	II	DMAc	TEA ^c	30 ^h	Water	92	0.191 ^g	-0.381 ^g
PAI ₂₉	III	NMP	Py	3 ^h	MeOH/Water	80	0.173 ^g	-0.000 ^g
PAI ₃₀	III	NMP	DBTDL	3 ^h	MeOH/Water	70	0.221 ^f	-0.421 ^f

^a Method I: Graduate heating at different temperature, Method II: Refluxing, Method III: Irradiating by a domestic microwave oven at 100% of its power.

^b N-methyl pyrrolidone.

^c Pyridine,

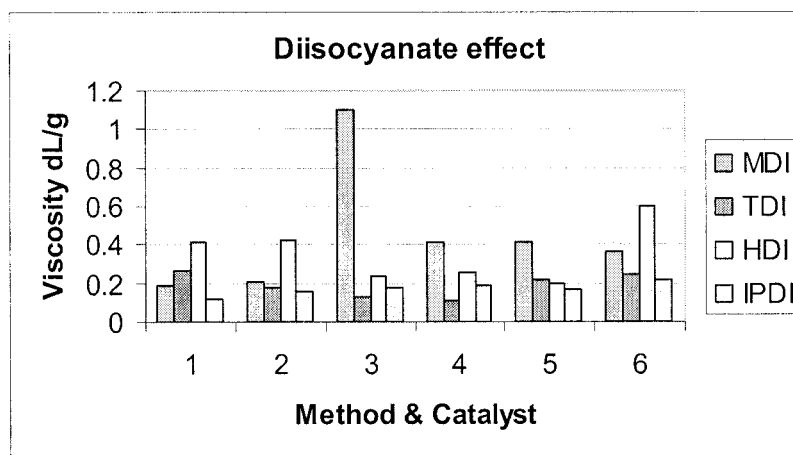
^d dibutyltin dilaurate,

^e triethylamine.

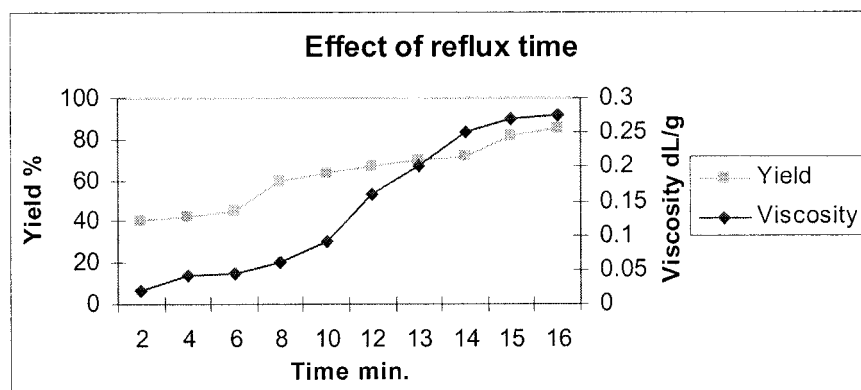
^f Measured at a concentration of 0.5 g/dL in DMF containing 2% W/W LiCl at 25°C.

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

^h Minute. A: 2 h 0°C, 2 h RT, 2 h 60°C, 2 h 80–90°C, 0.5 h 100°C.



Curve 5 Diisocyanate effect on the viscosity dL/g of PAIs in different methods and catalysts.



Curve 6 The effect of reflux time on the viscosity dL/g and yield % of PAI₂₂ for method II in the presence of TEA in DMAc.

viscosities and yields are comparable, but the highest viscosity was obtained in NMP and the lowest one in DMSO. Explanation for this difference lies in the higher solubility of the reaction mixture during the polymerization reaction period in NMP. In the case of DMSO, even at the beginning of the reaction the precipitation of oligomers occurred. In DMF and DMAc the precipitation of the growing polymer chains happened after heating the reaction mixture at 80–90°C for 2 h. Thus, NMP was selected as a solvent to study the effect of catalysts on viscosity in the case of method I.

In the case of method II, *o*-cresol, NMP, DMAc, and DMF were selected as solvents in the presence of DBTDL as a catalyst (Curve 2). In *o*-cresol, the reaction mixture had a limited solubility at RT, and during of refluxing became clear but, it precipitated after 1 min. In NMP the reaction mixture was soluble over the reaction period but, after 1 min turned to dark brown, thus low viscosity and yield could be related to very high boiling point of NMP and possibility of the chain scissioning of growing polymer chains. The reaction

mixture was soluble in DMF at RT, but after 1.5 min. reflux, a yellow precipitate was formed during heating. In the case of DMAc the reaction mixture was clear at RT and remained soluble under reflux condition up to 75 sec. When it was cooled up to RT a yellow precipitate was formed, which became clear again after reflux for overall heating time of about 2.5 min. Therefore, DMAc was selected as the best solvent for the fast reflux method because, during the reaction period (1-2 min) under reflux temperature, the reaction mixture was soluble and there was a possibility for polymer chains to grow well without any decomposition. In the case of other catalysts and no catalyst conditions, the best heating periods were selected in accord with the beginning of the precipitation of the growing polymer chains, or sudden increase in the viscosity of the reaction mixture (Table 1).

For the method III *o*-Cresol, NMP, DMAc, and DMF were also selected as solvents in the presence of Py as a catalyst. According to the Curve 3 the viscosities and yields in DMAc and DMF are comparable. The result in *o*-Cresol was relatively low, this could be explained

TABLE V
Solubility Properties of PAIs

Solvent	PAI ₅	PAI ₃	PAI ₁₃	PAI ₁₆	PAI ₂₃	PAI ₂₄	PAI ₂₅	PAI ₃₀
DMF	–	+++	+++	±	±	–	+++	±
2% LiCl-DMF	±	+++	+++	+++	+++	±	+++	+++
NMP	±	+++	+++	++	++	±	+++	++
2% LiCl NMP	±	+++	+++	+++	+++	±	+++	+++
DMAc	–	+++	+++	++	±	–	+++	±
<i>o</i> -Cresol	–	+++	+++	++	±	±	++	+
DMSO	–	++	++	+	±	±	++	±
MeOH	–	–	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–	–	–
Acetone	–	–	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–	–	–
Cyclohexane	–	–	–	–	–	–	–	–
THF	–	–	–	–	–	–	–	–

+, Soluble at boiling temperature, ++; Soluble at boiling water temperature, +++; Soluble at RT, ±; Partially soluble, –; nsoluble.

TABLE VI
¹H-NMR and FTIR Characterization of PAIs

PAI ₆	FTIR Peaks (cm ⁻¹): 3310 (m, br, NH v), 3230 (w), 3124 (w), 3060 (w), 2964 (w), 2950 (w), 2900 (w), 1780 (w, amide I non-H bonded), 1725 (s), 1685 (s), 1599 (s), 1540 (s, C—N v + NH amide II), 1520 (s), 1412 (s), 1380 (s), 1320 (m, C—N v + NH amide IV), 1313 (s), 1260 (s), 1173 (m), 1105 (w), 950 (m), 780 (m), 730 (w), 540 (w), 500 (w).	¹ H-NMR Peaks (ppm): 0.91 (d, CH ₃ , J = 6.21 Hz), 0.95 (d, CH ₃ , J = 6.18 Hz), 1.51 (s, CH, br), 1.89–2.27 (m, CH ₂), 3.81–3.84 (distorted m, CH ₂), 4.99–5.02 (distorted dd, CH), 7.09–8.52 (m, 19H Ar—H), 10.13–10.22 (s, br, NH), 10.84 (s, NH), 12.74 (s, br, terminal OH of the acid moiety).
PAI ₁₄	FTIR Peaks (cm ⁻¹): 3317 (m, br), 3200 (m, sh), 3150 (w), 2950 (m), 2924 (m), 2890 (w), 1790 (w), 1719 (s), 1690 (s), 1605 (s), 1532 (s), 1410 (s), 1380 (s), 1320 (m), 1252 (s), 1170 (m), 1100 (w), 840 (w), 760 (w), 710 (w), 500 (w, br).	
PAI ₂₂	FTIR Peaks (cm ⁻¹): 3304 (m, br), 3220 (w), 3080 (w), 2931 (s), 2880 (m), 1785 (m), 1725 (s), 1690 (s), 1605 (s), 1532 (s), 1475 (m), 1400 (s), 1370 (s), 1300 (s), 1259 (s), 1173 (s), 1090 (m), 850 (s), 760 (m), 710 (m), 500 (w, br).	
PAI ₂₇	FTIR Peaks (cm ⁻¹): 3344 (m, br), 3120 (w), 3070 (w), 2951 (m), 2925 (m, sh), 2790 (w, sh), 1780 (w), 1712 (s), 1605 (s), 1475 (w), 1379 (s), 1320 (m), 1252 (s), 1173 (m), 1100 (w), 850 (w), 760 (m), 720 (w), 500 (w, br).	

in terms of low solubility of the reaction mixture especially, at RT and during grinding. Considerable results were obtained in the case of NMP as a solvent (Table I). To find the best irradiation time at 100% power, the effect of time on the viscosity and yield of the polymers in the presence of Py as a catalyst and NMP as a solvent was studied (Curve 4). From this data it is clear that a gradual increase in the irradiation time from 2 to 3 min caused an increase in the viscosities and yields of the resulting PAIs. But more than 3 min irradiation imposed a reverse effect on viscosity, particularly on the yield. It could be inferred that, up to 3 min irradiation, chain extension of the growing polymer chains are being completed, but more irradiation caused a depolymerization reaction and chain scissioning. The same investigation was performed in the presence of DBTDL or TEA as a catalyst and without a catalyst conditions, respectively, to find the best irradiation time for each case (Table I). According to data pertaining to Table I, the shorter reaction time

is when Py has been used as a catalyst. It is note worthy to mention that the ratio of solvent to solid can affect the viscosities and yields of the PAIs. The best ratio that was obtained is 2–2.5 : 1 w/w of the solvent to the solid.

The polymerization reactions of monomer (5) with TDI, HDI, and IPDI were also carried out with the same fashion with three different methods according to the optimized solvents and catalysts for each method (Tables II–IV).

In the case of method I, NMP as the solvent and DBTDL as the catalyst and without a catalyst condition were chosen to investigate the outcome of this

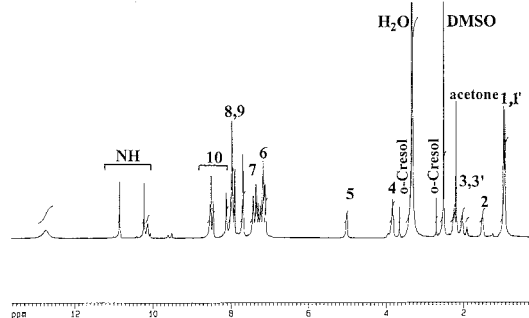
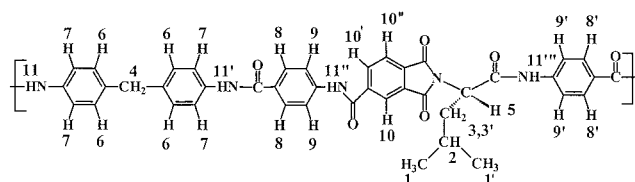


Figure 1 ¹H NMR (500 MHz) spectrum of PAI-based MDI in DMSO-*d*₆ at RT.

TABLE VII
 Elemental Analysis of PAIs^a

Polymer	Formula		C %	H %	N %
PAI ₁ (MDI)	C ₄₂ H ₃₅ N ₅ O ₆	Calcd.	71.78	4.99	9.92
	705.769 g/mol	Found	71.32	4.99	10.11
PAI ₁₃ (TDI)	C ₃₆ H ₃₁ N ₅ O ₆	Calcd.	68.67	4.96	11.12
	629.671 g/mol	Found	68.50	5.10	11.36
PAI ₂₄ (HDI)	C ₃₅ H ₃₇ N ₅ O ₆	Calcd.	67.40	5.98	11.22
	623.707 g/mol	Found	67.21	6.03	11.40
PAI ₂₆ (IPDI)	C ₃₉ H ₄₃ N ₅ O ₆	Calcd.	69.11	6.39	10.33
	677.799 g/mol	Found	69.00	6.51	10.55

^a The polymer sample was dried *in vacuo* at 100°C for 10 h.

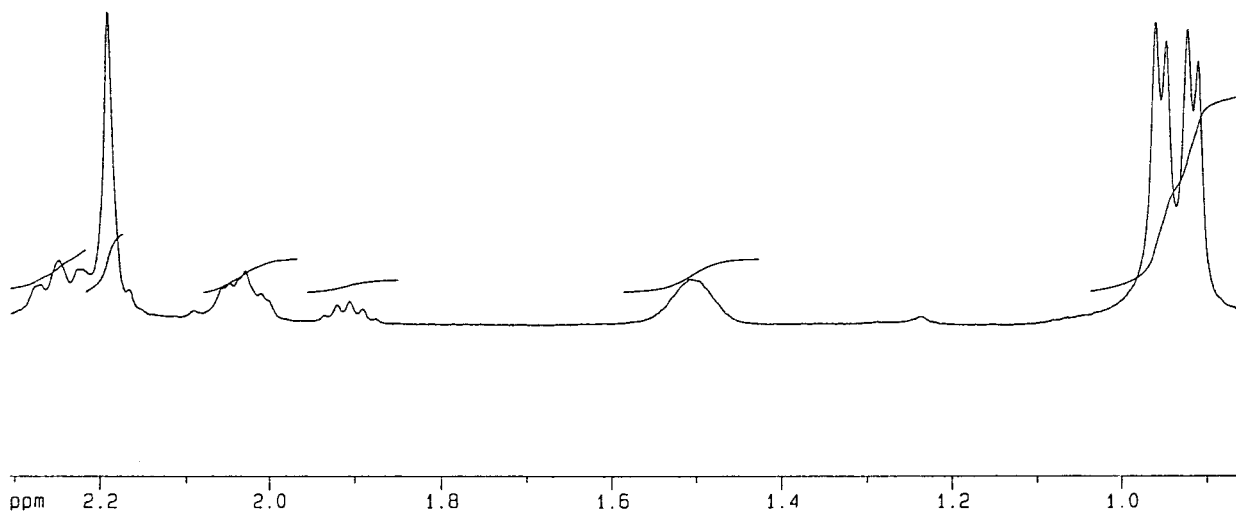


Figure 2 ^1H NMR (500 MHz) spectrum of PAI-based MDI in $\text{DMSO-}d_6$ at RT. Expanded region for the aliphatic protons # (H: 1–3) ($\delta = 0.91\text{--}1.27$ ppm).

method for the reaction of monomer (5) with other diisocyanates. According to Tables II–IV, PAIs-based HDI provided higher viscosities than the viscosities of

PAIs-based TDI or IPDI. It could be seen that the gradual heating method has comparable results for the polymerization reactions of (5) with MDI, TDI, and

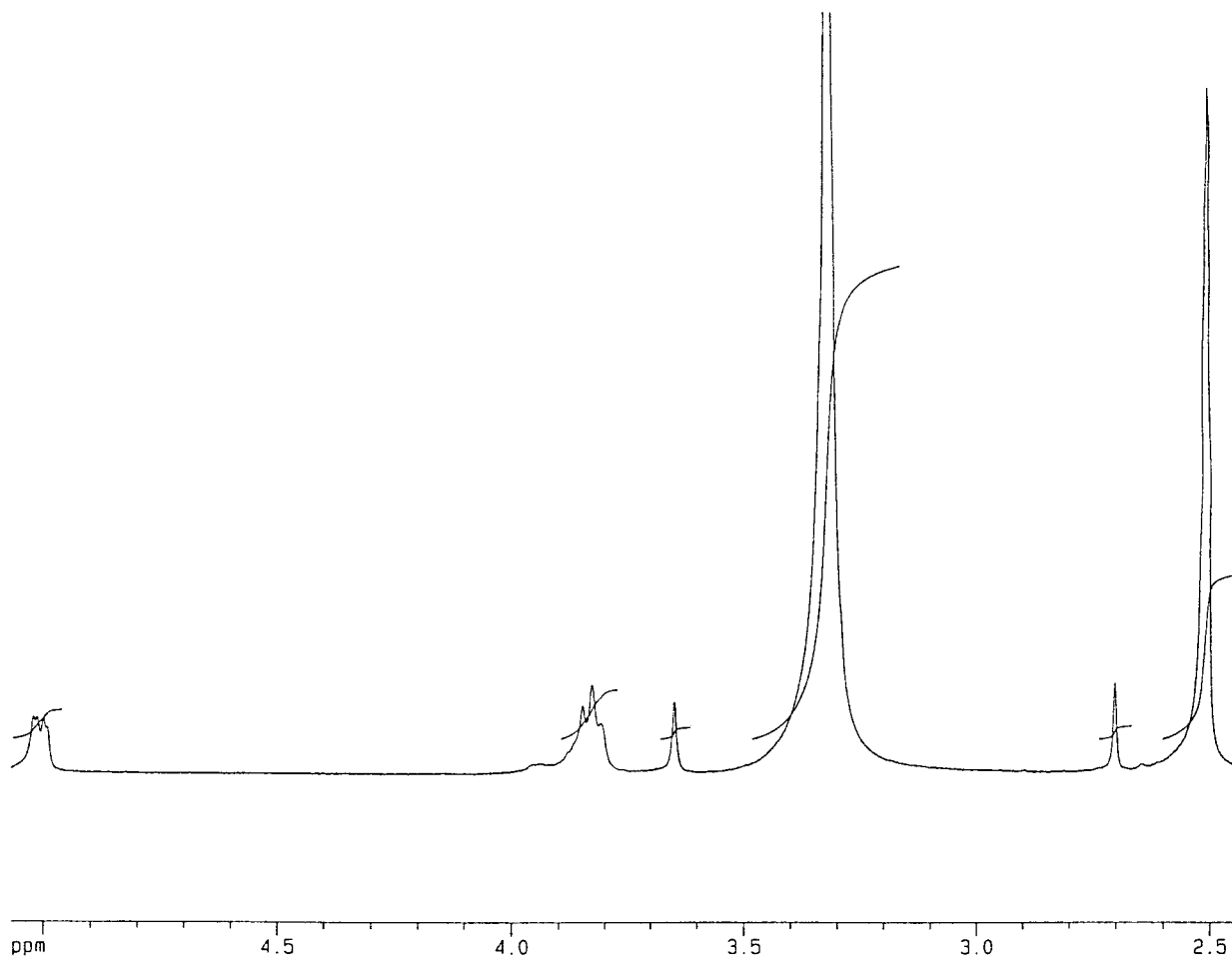


Figure 3 ^1H NMR (500 MHz) spectrum of PAI-based MDI in $\text{DMSO-}d_6$ at RT. Expanded region for the aliphatic protons # (H: 4–5) ($\delta = 2.51\text{--}5.02$ ppm).

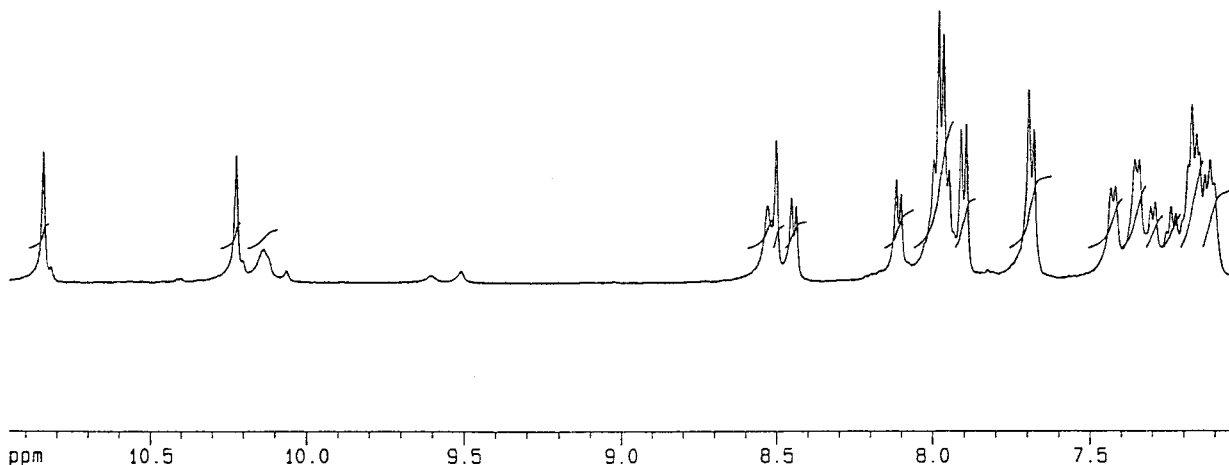


Figure 4 ^1H NMR (500 MHz) spectrum of PAI-based MDI in $\text{DMSO-}d_6$ at RT. Expanded region for aromatic protons and NH ($\delta = 7.09\text{--}10.84$ ppm).

IPDI, the cyclic rigid diisocyanates, but it shows a distinct effect on the polymerization of PAIs-based HDI, the linear aliphatic flexible diisocyanate (Curve 5, columns 1 and 2).

In method II, DMAc was used as a solvent and the reaction was performed in the presence of Py or TEA as a catalyst. The reaction time in each case was verified upon the precipitation of the polymers during heating (PAI_{15}), a sudden increase in the viscosity of the reaction mixture (PAI_{16}), precipitation of the reaction mixture after cooling up to RT after each 2 min heating-cooling intervals ($\text{PAI}_{21}\text{--}\text{PAI}_{22}$), or the ability to obtain a good precipitate in a nonsolvent ($\text{PAI}_{27,28}$). This means that, each definite time in Tables II–IV has been recognized as the least possible heating period that is necessary to obtain a suitable reaction product, without becoming gummy or lack of precipitation in methanol or water. Curve 6 shows this study to verify the optimized heating time, for obtaining a suitable reaction product for PAI_{22} as an example.

According to Curve 5 for method II, the best results in terms of shorter heating periods and higher viscosities were obtained for PAIs-based MDI, the symmetric rigid more thermally stable diisocyanate, in comparison with the other selected diisocyanates (Table I, Curve 5, columns 3 and 4). Under reflux condition the unsymmetric diisocyanates such as TDI and IPDI exhibit lower viscosities, compared to the symmetric MDI and HDI. This could pertain to the better possibility of chain arrangement and chain growth, when a step-growth polymerization reaction mechanism is performed during a limited reaction time.

In method III, NMP was used as a solvent in the presence of Py or DBTDL as a catalyst, respectively, for the polymerization reaction. The reaction mixture was irradiated in a microwave oven at 100% of its power for a fixed time (3 min). Upon the reported viscosities in Tables I–IV, the effect of Py as the reac-

tion catalyst is relatively comparable with TDI, HDI, and IPDI, but there is a great effect on the viscosity of the PAI-based MDI at the same reaction. In the presence of TEA as a catalyst, comparable viscosities are obtained for PAIs-based MDI, TDI, and IPDI, but a remarkable effect is observed for PAI-based HDI.

The solubility properties of PAIs were studied in different solvents (Table V). The polymers are soluble in amide type solvents such as NMP, DMF, DMAc, and to some extent in *o*-cresol and DMSO. They are insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

Structural characterization of PAIs

The resulting polymers were characterized by FTIR spectroscopy, ^1H NMR spectroscopy, and elemental analyses. The results are shown in Tables VI and VII.

The ^1H NMR spectrum of PAI-based MDI showed peaks that confirms its chemical structure (Figs. 1–4). It showed peaks for CH_3 (1), (1'), which appeared as doublets according to their coupling with H (2) with $J = 6.21$ Hz and $J = 6.18$ Hz in the region of 0.90–0.95 ppm. Peaks in the region of 1.50–2.27 ppm are related to H (2) and the diastereotopic hydrogens of CH_2 (3, 3'), which appeared as a multiplet. Peaks in the region of 3.80–3.84 and 4.99–5.02 ppm pertain to CH_2 (4) and CH (5), respectively. The aromatic protons appeared in the region of 7.09–8.52 ppm, where peaks in the region of 8.11–8.52 ppm are related to TMA aromatic ring moiety. The peaks in the region of 10.13–10.84 ppm are assigned for the N–H bond of the amide groups.

The FTIR spectrum of PAIs showed peaks, which confirms their chemical structure. As an example, the FTIR spectrum of $\text{PAI}_6\text{--MDI}$ (Fig. 5) showed that the characteristic absorptions of amide and imide groups

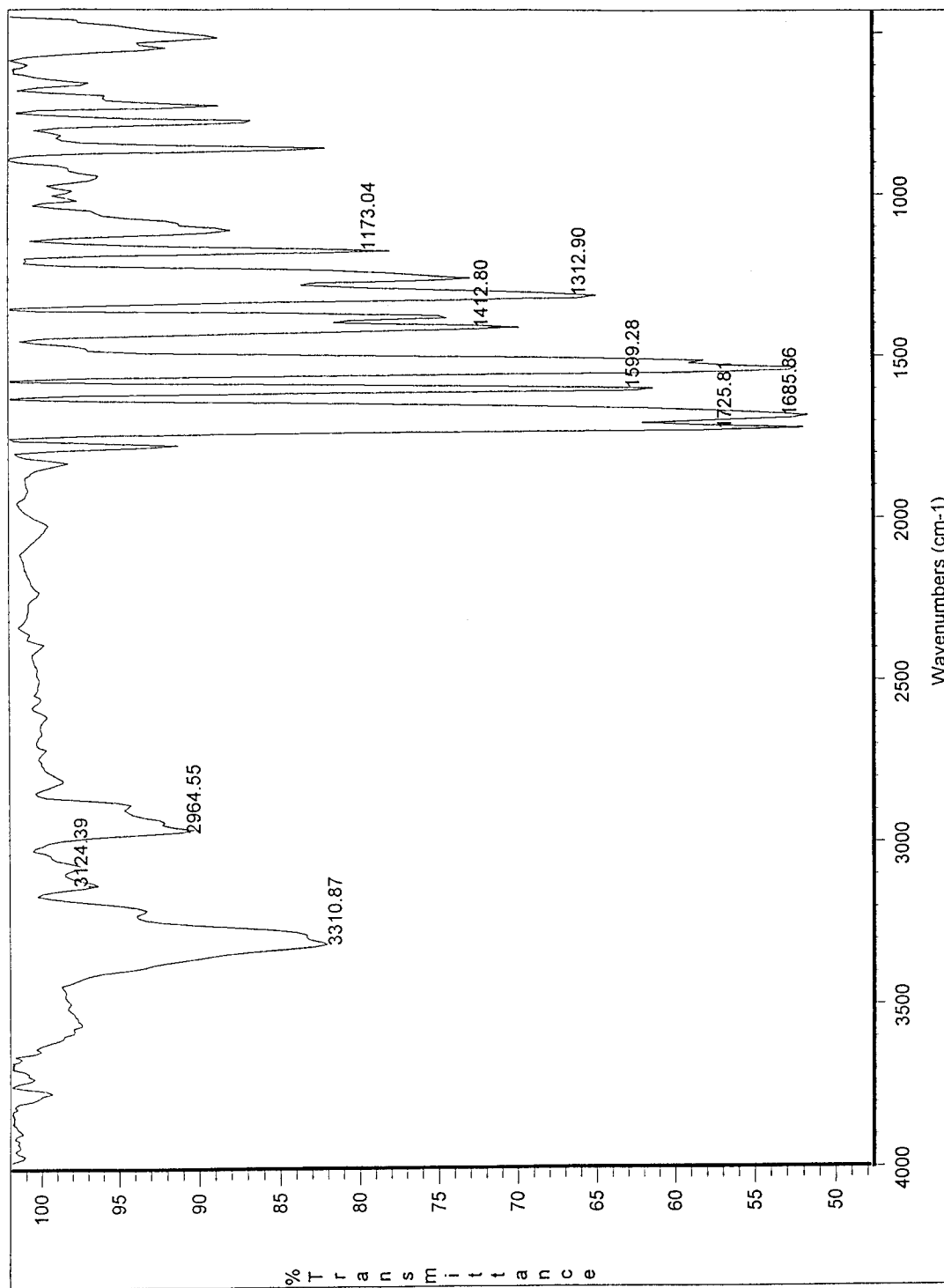
Figure 5 FTIR (KBr) spectrum of polymer PAI₆.

TABLE VIII
Thermal Properties of PAIs (24, 5)

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
PAI ₅	260	280	49
PAI ₂₄	185	220	27

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 30°C/min. in air.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 30°C/min. in air.

^c Percentage weight of material left undecomposed after TGA analysis at a temperature of 500°C in air.

occurred around 3310, 1780, 1725, 1685, and 1540 cm^{-1} , peculiar to N—H stretching and C=O stretching of imide and amide groups, respectively. Peaks at 1412, 1313, 780, and 730 cm^{-1} show the presence of the imide heterocyclic ring in the polymer.

The elemental analyses results are also in good agreement with calculated percentages of carbon, hydrogen, and nitrogen contents in the polymer repeating units (Table VII).

Thermal properties

Thermal properties of PAI₅ (MDI) and PAI₂₄ (HDI) were evaluated with TGA and DSC under an air atmosphere (Table VIII).

The thermal stability of the PAIs was evaluated by thermogravimetric analyses. The 5 and 10% weight

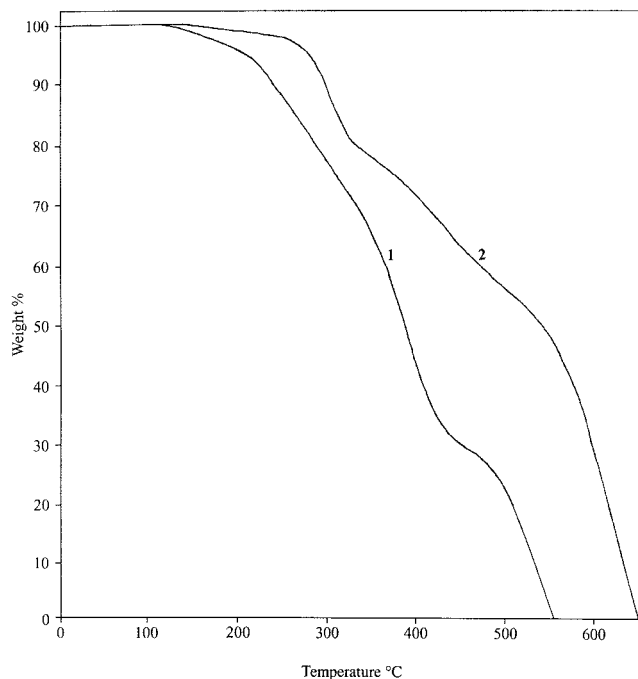


Figure 6 TGA thermograms of PAI₂₄-HDI (1) and PAI₅-MDI (2) under air atmosphere at a heating rate of 30°C/min.

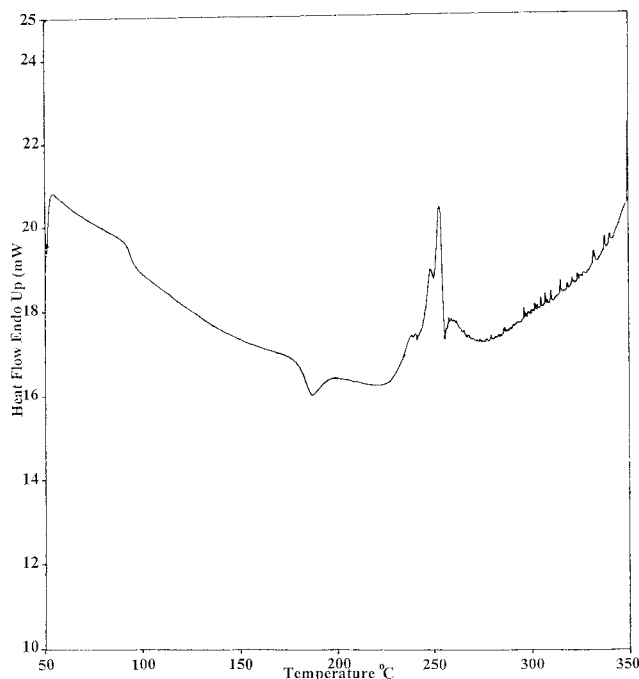


Figure 7 DSC curve of PAI₂₄ (HDI) under air atmosphere.

loss (T_5 , T_{10}) of the polymers and residue at 500°C (char yield) were used as criterions for their thermal stability. According to Table VIII, it is clear that the PAI-based aromatic isocyanate has higher thermal stability than the PAI-based aliphatic isocyanate (Fig. 6)

The thermal behavior of PAI₂₄, as an example, was studied by DSC. No transition associated with softening or melting was observed, although a glass transition temperature (T_g) was observed around 95°C. It showed an exotherm around 186°C, which was assigned to its thermal degradation in accordance with the TGA thermogram, and showed an endotherm ranging from 224–280°C that is in agreement with T_5 in the TGA thermogram (Fig. 7).

CONCLUSIONS

This is the first time that moderate to high molecular weight optically active PAIs were synthesized from direct polycondensation reaction of a chiral dicarboxylic acid having a pre-formed imide ring and different diisocyanates according to the isocyanate route under microwave irradiation as well as conventional solution methods. Moreover, in comparison with common methods for preparation of polyamides, we omit one stage for preparing diacyl chloride from diacid, and use of carcinogenic diamines in our method. According to Curve 5, it could be concluded that the best results were obtained for the reaction of monomer (5) with MDI (6) by method II in the presence of Py, then for HDI by method III in the presence of DBTDL, for TDI by method III in the presence of DBTDL, and in

the case of IPDI, by method III in the presence of DBTDL, subsequently. Therefore, microwave irradiation has been a suitable method for preparation of PAIs by the diisocyanate route.

We thank Miss. M. Youssefi and Mr. M. Shojaei (the Research Institute of Petroleum Industry, Tehran, I.R. Iran) for recording TGA and DSC data. Useful help from Miss. Z. Rafiee (IUT) is also acknowledged.

References

1. Akekah, A.; Sherrington, D. C. *Chem Rev* 1981, 81, 557.
2. Aglietto, M.; Chiellini, E. D.; Antone, S.; Ruggeri, G.; Solaro, R. *Pure Appl Chem* 1988, 60, 415.
3. Yuki, H.; Okamoto, Y.; Okamoto, I. *J Am Chem Soc* 1980, 102, 6358.
4. Okamoto, Y.; Yashima, E. *Angew Chem Int Ed Engl* 1999, 37, 1020.
5. Soai, K.; Niwa, S. *Chem Rev* 1992, 92, 833.
6. Wulff, G. *Angew Chem Int Ed Engl* 1989, 28, 21.
7. Ciardelli, F. *Encycl Polym Sci Eng* 1987, 10, 463.
8. Farina, M. *Top Stereochem* 1987, 17, 1.
9. Fontaille, M.; Guyot, A. In *Recent Advances in Synthetic and Mechanistic Aspect of Polymerization*; Kluwer Academic: Dordrecht, The Netherlands, 1987.
10. Murata, H.; Sanda, F.; Endo, T. *J Polym Sci Part A Polym Chem* 1998, 36, 1679.
11. Sanda, F.; Endo, T. *Macromol Chem Phys* 1999, 200, 2651.
12. (a) Methenitis, C.; Morcellet, J.; Morcellet, M. *Polym Bull (Berlin)* 1984, 181, 485; (b) Methenitis, C.; Morcellet, J.; Morcellet, M. *Polym Bull (Berlin)* 1984, 12, 141.
13. (a) Murata, H.; Sanda, F.; Endo, T. *Macromolecules* 1996, 29, 5535; (b) Katakai, R.; Nakayama, Y. *J Chem Soc Chem Commun* 1977, 22, 805; (c) Murata, H.; Sanda, F.; Endo, T. *Macromolecules* 1997, 30, 2902; (d) Sanda, F.; Ogawa, F.; Endo, T. *Polymer* 1998, 39, 5543; (e) Sanda, F.; Kamatani, J.; Handa, H.; Endo, T. *Macromolecules* 1999, 32, 2490; (f) Kudo, H.; Sanda, F.; Endo, T. *Macromol Chem Phys* 1999, 200, 1232.
14. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S.; Sheikholeslami, B. *Polym Int* 1998, 47, 193.
15. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoee, S. *J Polym. Sci Part A Polym Chem* 1999, 37, 1211.
16. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Rafiemanzelat, F. *Polym Int* 1999, 48, 169.
17. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *Polym Int* 1999, 48, 1133.
18. Mallakpour, S. E.; Hajipour, A. R.; Roohipour Fard, R. *Eur Polym J* 2000, 36, 2455.
19. Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *J Polym Sci Part A Polym Chem* 2002, 22, 177.
20. Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *Eur Polym J* 2002, 38, 475.
21. Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *Polym Sci Ser A* 2002, 44, 243.
22. Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *J Polym Sci Part A* 2003, 41, 1077.
23. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Application*; Marcel Dekker: New York, 1996; p 49.
24. Yi, M. H.; Jin, M. Y.; Choi, K. Y. *Angew Makromol Chem* 1955, 233, 89.
25. Lin, J. H.; Yang, C. P. *J Polym Sci Part A Polym Chem* 1996, 34, 747.
26. Avella, N.; Maglio, G.; Palumbo, R. *J Polym Sci Part A Polym Chem* 1996, 34, 1219.
27. Patel, H. S.; Mathur, A. B.; Bhardwaj, I. S. *J Macromol Sci Pure Appl Chem* 1995, A32, 2025.
28. Kricheldorf, H. R.; Gurau, M. *J Macromol Sci Pure Appl Chem* 1995, A32, 1831.
29. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Polym Sci Polym Chem Ed* 2000, 38, 1154.
30. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *Eur Polym J* 2002, 38, 2011.
31. Liaw, D. J.; Hsu, P. N.; Liaw, B. Y. *J Polym Sci Part A Polym Chem* 2001, 39, 63.
32. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Part A Polym Chem* 1985, 23, 2077.
33. Ray, S.; Rao, Y. V.; Bhattacharya, V. K.; Maiti, S. *Polym J* 1983, 15, 169.
34. Das, S.; Maiti, S. *Makromol Chem Rapid Commun* 1980, 1, 403.
35. Ray, A.; Das, S.; Maiti, S. *Makromol Chem Rapid Commun* 1981, 2, 333.
36. Nieto, J. L.; de La Campa, J. G.; de Adajo, J. *Makromol Chem* 1982, 183, 557.
37. de La Campa, J. G.; de Abajo, J.; Nieto, J. L. *Makromol Chem* 1982, 183, 571.
38. Otsuki, T.; Kakimoto, M.A.; Imai, Y. *J Appl Polym Sci* 1990, 40, 1433.
39. Zdrachala, R. J.; Firer, E. M.; Fellers, J. F. *J Polym Sci Polym Chem Ed* 1977, 15, 689.
40. Castaldo, L.; Maglio, G.; Palumbo, R. *Polym Sci Polym Chem Lett Ed* 1978, 16, 643.
41. Raab, M.; Masar, B.; Kolarik, J.; Cefelin, P. *Int J Polym Mater* 1979, 7, 219.
42. Rasmussen, J. K.; Smith, H. K, II. *J Appl Polym Sci* 1983, 28, 2473.
43. Ogata, N.; Yui, N. *J Macromol Sci-Chem* 1984, A21, 1097.
44. de Candia, F.; Petrocelli, V.; Russo, R.; Maglio, G.; Palumbo, R. *Polymer* 1986, 27, 797.
45. Imai, Y.; Kajiyama, M.; Ogata, S.; Kakimoto, M. *Polym J* 1984, 16, 267.
46. Imai, Y.; Kajiyama, M.; Ogata, S.; Kakimoto, M. *Polym J* 1984, 17, 1173.
47. Otsuki, T.; Kakimoto, M. A.; Imai, Y. *Makromol Chem Rapid Commun* 1987, 8, 637.
48. Ulrich, H. *Chemistry and Technology of Isocyanates*; J Wiley & Sons: Chichester, 1996.
49. Gedye, R.; Smith, F.; Westaway, H. A.; Baldiseria, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett* 1986, 27, 279.
50. Abramovich, R. A. *Org Prep Proceed Int* 1991, 23, 683.
51. Limousin, C.; Cleophax, J.; Loupy, A.; Petti, A. *Tetrahedron* 1998, 54, 13567.
52. Loupy, A.; Regnier, S. *Tetrahedron Lett* 1999, 40, 6221.
53. Chtti, S.; Bortolussi, M.; Loupy, A.; Blais, J. C.; Bogdal, D.; Majdoub, M. *Eur Polym J* 2002, 38, 1851.
54. Hajipour, A. R.; Mallakpour, S. E.; Khoee, S. *Synlett* 2000, 5, 740.
55. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Polym Sci Polym Chem Ed* 2000, 38, 1154.
56. Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Polym Int* 2000, 49, 1383.
57. Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Eur Polym J* 2001, 37, 119.
58. Mallakpour, S. E.; Hajipour, A. R.; Vahabi, R. *Iranian Polym J* 2001, 10, 321.
59. Mallakpour, S. E.; Hajipour, A. R.; Vahabi, R. *J Appl Polym Sci* 2002, 84, 35.