

ORIGINAL ARTICLE

Molten salt-supported polycondensation of optically active diacid monomers with an aromatic thiazole-bearing diamine using microwave irradiation



Shadpour Mallakpour ^{a,b,*}, Amin Zadehnazari ^a

^a *Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran*

^b *Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran*

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ABSTRACT

Microwave heating was used to prepare optically active thiazole-bearing poly(amide-imide)s. Polymerization reactions were carried out in the molten tetrabutylammonium bromide as a green molten salt medium and triphenyl phosphite as the homogenizer. Structural elucidation of the compounds was performed by Fourier transform infrared and NMR spectroscopic data and elemental analysis results. The polymeric samples were readily soluble in various organic solvents, forming low-colored and flexible thin films via solution casting. They showed high thermal stability with decomposition temperature being above 360 °C. They were assembled randomly in a nanoscale size.

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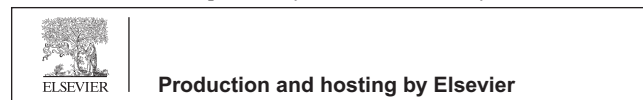
Introduction

Recently, microwave technology has developed rapidly in the field of chemical analysis and synthesis and become an impor-

* Corresponding author Tel.: +98 311 391 3267; fax: +98 311 391 2350.

E-mail addresses: mallak@cc.iut.ac.ir, mallakpour84@alumni.ufl.edu, mallak777@yahoo.com (S. Mallakpour).

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tant component in combinatorial and green chemistry [1]. The application of microwave irradiation to provide the energy for the activation of chemical species certainly leads to faster and cleaner reactions when compared to conventional heating. Compared with conventional heating, microwave irradiation has a more homogeneous heating process. Moreover, it can promote nucleation and reduce the synthesis time significantly and offer numerous advantages over conventional heating such as noncontact heating (reduction of over-heating of material surfaces), energy transfer instead of heat transfer (penetrative radiation), material-selective and volumetric heating, fast start-up and stopping, and last, but not least, a reverse gradient as heat starts to build up from the interior (core) of

the material body [2–5]. Although microwave heating is already an established technique in organic chemistry, a number of polymers and polymeric materials can also be successfully prepared, cross-linked, and processed under microwave irradiation [6–9]. Consequently, not only the problem of pollution can be overcome, but the risk of overpressure and explosions can also be avoided.

In recent times, molten ionic salts such as molten tetrabutylammonium bromide (TBAB) have been used very effectively for various reactions because of their solvating ability, simple workup procedure, and recyclability. TBAB is highly polar but noncoordinating and catalyzes the reactions, giving better selectivity [10–14]. Moreover, it being ionic in character, coupled to microwave irradiation efficiently and consequently may be ideal for microwave-absorbing entities for several organic reactions as well as polymerization processes. A recent review [8] presents studies on applications of molten TBAB to microwave-assisted polymerization reactions, showing its ever-increasing importance.

The use of optically active soluble macromolecule has attracted much attention of chemists because of their high potential applications as catalysis for asymmetric syntheses, enantiomeric separation, and chiral sensing [15–17]. The common way to prepare a chiral polymer is to attach only one chiral group per polymer. In the polycondensation reactions, we use natural amino acids as chiral inducting agents [18]. Chiral polymers containing amino acids are of great interest in scientific research and technological innovation because they are expected to be nontoxic and can be employed for biomedical applications [19–21]. Furthermore, a high degree of amino acid functionality can lead to polymers with increased solubility and the ability to form secondary structures [22].

The main aim of this work is to accelerate microwave irradiation-assisted polycondensation reaction of optically active diacids with a thiazole-bearing diamine in a medium consisting of molten TBAB and to investigate the physico-chemical characterization of the obtained polymers. Moreover, the properties of these synthesized polymers such as solubility, optical behavior, thin film forming ability, thermal stability, and microstructural observations will be addressed.

Experimental

Starting materials

Commercially available 2-aminothiazole, 3,5-dinitrobenzoylchloride, acetone, hydrazine hydrochloride, FeCl_3 , propylene oxide, trimellitic anhydride, natural amino acids (S-valine, L-leucine, L-methionine, and L-isoleucine), glacial acetic acid, TBAB, and triphenyl phosphite (TPP) were used as received without further purification. These chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Germany), and Merck Chemical Co. (Germany). N,N' -dimethylacetamide (DMAc) ($d = 0.94 \text{ g cm}^{-3}$ at 20°C) and N,N' -dimethylformamide (DMF) ($d = 0.94 \text{ g cm}^{-3}$ at 20°C) were distilled over barium oxide under the reduced pressure prior to use.

Measurements

The apparatus used for the step-growth polymerization reactions was a Samsung microwave oven (2450 MHz, 900 W, Republic of Korea).

Melting points of the monomers were measured on a melting-point apparatus (Gallenham, England) without correction.

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (Germany) Avance 500 instrument at room temperature (RT) in dimethylsulfoxide- d_6 (DMSO- d_6). Multiplicities of proton resonance were designated as singlet (s), doublet (d), triplet (t), and multiplet (m). ^{13}C spectrum is broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and stated relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR.

Fourier transform infrared (FT-IR) spectra were recorded on a spectrophotometer (Jasco-680, Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br).

Elemental analysis was performed in an Elementar Analysensysteme GmbH, Germany.

Ultraviolet maximum wavelength (λ_{max}) values were determined with an ultraviolet-visible (UV-vis) spectrophotometer, JASCO, V-570, Japan, in DMAc at a concentration of $10^{-5} \text{ mol L}^{-1}$ at RT.

Inherent viscosities were measured using a Cannon Fenske Routine Viscometer (Germany) at the concentration of 0.5 g/dL in DMF at 25°C .

Optical specific rotations were measured at the concentration of 0.5 g/dL in DMF at 25°C using a quartz cell (1.0 cm) with a Jasco Polarimeter (JASCO Co., Ltd., Japan).

Thermogravimetric analysis (TGA) is performed with a STA503 win TA (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) at a heating rate of $20^\circ\text{C min}^{-1}$ from 25°C to 800°C under nitrogen atmosphere.

The X-ray diffraction (XRD) patterns of polymers were recorded using an XRD (Bruker, D8ADVANCE, Germany) with a copper target at 40 kV and 35 mA and $\text{CuK}\alpha$ $\lambda = 1.54 \text{ \AA}$ in the range $10\text{--}90^\circ$ at the speed of $0.05^\circ \text{ min}^{-1}$.

The morphology of the polymers was observed using field emission scanning electron microscopy (FE-SEM) (HITACHI S-4160, Japan). The effect of ultrasound energy on the size of polymer particles was investigated by MISONIX ultrasonic liquid processors, XL-2000 SERIES, USA. Ultrasound was a wave of frequency $2.25 \times 10^4 \text{ Hz}$ and power 100 W.

Monomer synthesis

Synthesis of 3,5-diamino-*N*-(thiazol-2-yl)benzamide (4)

Iron oxide hydroxide catalyst was prepared according to the literature [23]. 3,5-dinitro-*N*-(thiazol-2-yl)benzamide (3) was also prepared according to the reported procedure [24]. To a suspension of the purified 3,5-dinitro-*N*-(thiazol-2-yl)benzamide (1.0 g, 3.4 mmol) and iron oxide hydroxide (0.1 g, 1.13 mmol) in methanol (15 mL), hydrazine monohydrate (1.5 mL) was added dropwise to the stirred mixture at 60°C within 10 min. After complete addition, the mixture was heated at the reflux temperature for another 12 h. The reaction

solution was filtered hot to remove iron oxide hydroxide, and the filtrate was then filtered cold to remove the solvent. The crude product was purified by recrystallization from methanol to give 0.68 g of diamine 4 as brown needles (68% yield, m.p. = 208–210 °C) [25].

FT-IR (KBr; cm^{-1}): 3434 (s, N–H stretch), 3385 (s, N–H stretch), 3103 (w, C–H aromatic), 1662 (s, C=O amide stretch), 1560 (m), 1525 (m), 1459 (w), 1326 (w), 1161 (w, C–O stretch), 830 (m), 779 (w, N–H out-of-plane bending). ^1H NMR (DMSO- d_6 ; δ , ppm): 4.907 (s, 4H, 2NH_2), 6.060 (s, 1H, Ar–H), 6.454 (s, 2H, Ar–H), 7.199–7.208 (d, 1H, Ar–H, $J = 3.60$ Hz), 7.449–7.507 (d, 1H, Ar–H, $J = 3.20$ Hz), 11.823 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 ; δ , ppm): 102.55 (CH, Ar), 103.01 (CH, Ar), 113.39 (CH, thiazole ring), 133.61 (C, Ar), 137.66 (CH, thiazole ring), 149.20 (C, Ar), 158.57 (C, Ar), 166.45 (C, C=O). Elemental analysis: calculated for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_5\text{S}$: C, 51.27%; H, 4.30%; N, 23.91%; S, 13.69%; found: C, 51.40%; H, 4.330%; N, 23.87%; S, 13.54%.

Preparation of imide-acid monomers

N-trimellitylimido-L- α -amino acids were prepared according to the previous works [18].

Polymerization

The one-step polycondensation reaction of equimolar amounts of diamine 4 and diacids (7a–7d), using molten TBAB as a reaction medium and TPP as a homogenizer, gave the poly(amide-imide)s (PAIs). A typical experimental procedure for polymerization reaction is given as follow: A mixture of 0.10 g (0.34 mmol) of N-trimellitylimido-S-valine (7a), 0.08 g (0.34 mmol) of diamine 4, and 0.44 g of TBAB (1.36 mmol) was placed in a porcelain dish and ground completely for 5 min; then, 0.23 mL (1.36 mmol) of TPP was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for 240 s at 100% of power level (900 W). The resulting viscous solution was poured into 30 mL of methanol, filtered, and dried at 80 °C for 6 h under vacuum to give 0.17 g (94%) of yellow powder PAI8a. The optical specific rotation was measured ($[\alpha]_{\text{Na},589}^{25} = -32.29$) at a concentration of 0.5 g/dL in DMF at 25 °C. The inherent viscosity was also measured ($\eta_{\text{inh}} = 0.48$ dL/g) at the same conditions.

PAI8a: Elemental analysis: calculated for $(\text{C}_{24}\text{H}_{19}\text{N}_5\text{O}_5\text{S})_n$: C, 58.90%; H, 3.91%; N, 14.31%; S, 6.55%. Found: C, 59.12%; H, 3.47%; N, 14.09%; S, 6.23%.

PAI8b: FT-IR (KBr, cm^{-1}): 3412 (m, br, N–H stretch), 3105 (w, C–H aromatic), 2957 (w, C–H aliphatic), 1777 (m, C=O imide, asymmetric stretching), 1718 (s, C=O imide, symmetric stretching), 1672 (m, C=O amide, stretching), 1602 (s), 1546 (m), 1450 (s), 1375 (m, CNC axial stretching), 1200 (m, CNC transverse stretching), 1069 (m), 726 (s, CNC

out-of-plane bending), 691 (w). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 0.92–0.94 (d, 6H, $J = 7.2$ MHz), 1.38–1.58 (m, 1H), 2.04–2.06 (dd, 2H, distorted), 5.02–5.04 (t, 1H, distorted), 7.25 (s, 1H, Ar–H), 7.55 (s, 1H, Ar–H), 7.98 (s, 1H, Ar–H), 8.13–8.17 (d, 2H, distorted), 8.19–8.26 (d, 2H, Ar–H, distorted), 8.61 (s, 1H, Ar–H), 10.25 (s, 1H, NH), 10.91 (s, 1H, NH), 12.72 (s, 1H, NH) ppm.

Elemental analysis: calculated for $(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_5\text{S})_n$: C, 59.63%; H, 4.20%; N, 13.91%; S, 6.37%. Found: C, 59.15%; H, 3.99%; N, 13.56%; S, 6.38%.

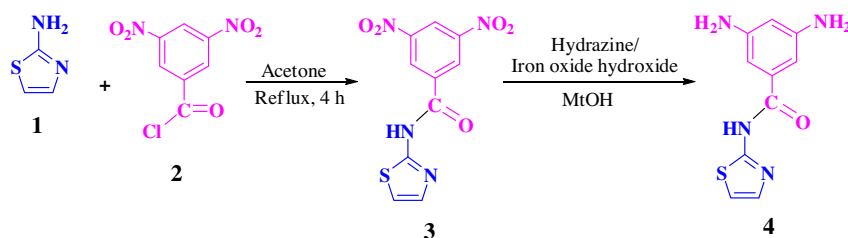
PAI8c: FT-IR (KBr, cm^{-1}): 3480 (m, br, N–H stretch), 3103 (w, C–H aromatic), 2964 (w, C–H aliphatic), 1777 (m, C=O imide, asymmetric stretching), 1719 (s, C=O imide, symmetric stretching), 1671 (m, C=O amide, stretching), 1602 (s), 1541 (m), 1451 (s), 1375 (m, CNC axial stretching), 1202 (m, CNC transverse stretching), 1086 (m), 724 (s, CNC out-of-plane bending), 620 (w).

PAI8d: FT-IR (KBr, cm^{-1}): 3445 (m, br, N–H stretch), 3100 (w, C–H aromatic), 2961 (w, C–H aliphatic), 1776 (m, C=O imide, asymmetric stretching), 1719 (s, C=O imide, symmetric stretching), 1670 (m, C=O amide, stretching), 1602 (s), 1542 (m), 1486 (s), 1375 (m, CNC axial stretching), 1201 (m, CNC transverse stretching), 1072 (m), 724 (s, CNC out-of-plane bending), 630 (w).

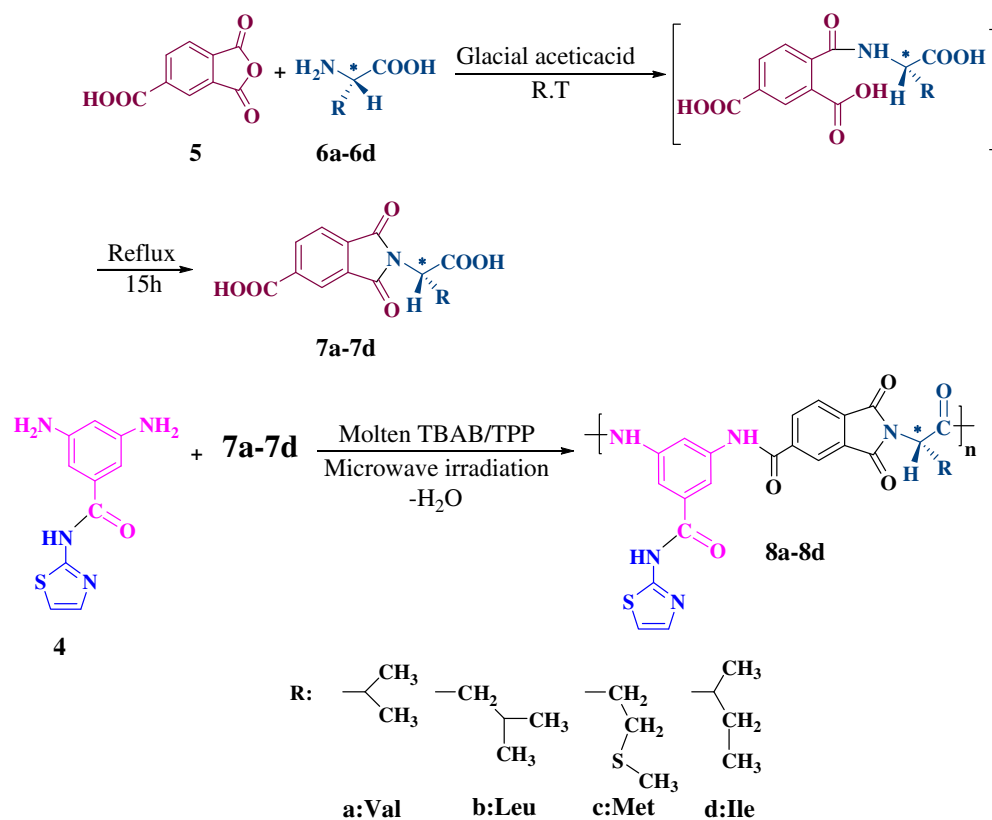
Results and discussion

Synthesis and structural characterization of monomers

Diacid monomers were synthesized by the condensation reaction of an equimolar amount of pyromellitic dianhydride and different amino acids in the reflux acetic acid solution [18]. Scheme 1 shows the synthetic route to 3,5-diamino-N-(thiazol-2-yl)benzamide using a two-step process. In the first step, nucleophilic displacement of 2-aminothiazole with 3,5-dinitrobenzoylchloride in acetone solvent resulted in 3,5-dinitro-N-(thiazol-2-yl)benzamide as a pale yellow solid [24]. In the second step, this dinitro compound was reduced in methanol in the presence of hydrazine hydrate and a catalytic amount of iron oxide hydroxide at 60 °C to produce brown crystals of the diamine 4. The structure of the diamine 4 was identified by elemental analysis, FT-IR, and NMR spectroscopic methods. In the FT-IR spectrum of diamine 4, the peak attributed to the stretching vibration of the bond C=O appeared at 1662 cm^{-1} . The absorption peaks of amine functions are obvious as two peaks at 3434 and 3385 cm^{-1} . In the ^1H NMR spectrum of diamine 4, the signals of aromatic protons appear in the range of 6.060–7.507 ppm, and the characteristic resonance signal at 4.907 ppm is due to the amino group. Moreover, the proton for the amide group is observed at 11.823 ppm.



Scheme 1 Synthesis of diamine 4.



Scheme 2 Synthetic route to the optically active diacids and PAIs.

Furthermore, in the ^{13}C NMR spectrum, seven peaks corresponding to the seven kinds of aromatic carbons appeared in the range of 102.55–158.57 ppm. This spectrum also exhibited a peak for carbonyl of amide group at 166.45 ppm.

Polymer synthesis

In view of our attention in microwave-assisted reactions and the importance of ionic liquids as solvents [8,26], we decided to use them in combination as a fast, simple, safe, and efficient method for step-growth polymerization of several natural amino acid-based diacids (7a–7d) with an aromatic thiazole-based diamine (4) (Scheme 2). The molten TBAB salt was selected because it proved to be the most valuable among those employed in our recent works [27–29]. The effect of microwave power levels and the period of heating were examined to provide the optimum reaction conditions. A series of experiments was performed with different reaction times under microwave irradiations. It was revealed that the optimal results were obtained after 240 s at 100% of power level. At higher radiation

times, dark products were obtained. On the other hand, under low radiation times, reactions gave low yields and inherent viscosities. This problem could be explained by the fact that molten TBAB salt is highly polar medium and likely to be a strong microwave absorption. The polymerization reactions of monomer 4 with diacids 7b–7d were also carried out with the same procedure according to the optimized conditions. The syntheses and some physical properties of these new PAIs (8a–8d) are given in Table 1. All the polymers were obtained in high yields (90–94%), and the inherent viscosities were 0.43–0.48 dL g^{-1} , as measured in DMF solutions. Also, the resulting polymers showed a yellow color. All of them are also optically active because they have a chiral center from amino acid in their main chain. The structure of the PAIs was confirmed by FT-IR and ^1H NMR spectroscopy and elemental analysis technique.

Polymer structure

The polymers were characterized by FT-IR and NMR spectrometers. Strong absorption bands in the FT-IR spectra are

Table 1 Synthesis and some physical properties of PAI8a–PAI8d prepared in the molten TBAB under microwave irradiation.

Diacid	Polymer ^a	Yield (%)	Inherent viscosity ^b (dL/g)	$[\alpha]_{\text{Na},589}^{25}$ ^b	$[\alpha]_{\text{Hg}}^{25}$ ^c	Color
7a	PAI8a	94	0.48	–32.29	–24.38	Yellow
7b	PAI8b	91	0.45	–30.08	–21.48	Yellow
7c	PAI8c	90	0.43	–35.56	–20.76	Yellow
7d	PAI8d	92	0.46	–34.14	–21.50	Yellow

^a Polymers were precipitated in methanol.

^b Measured at a concentration of 0.5 g dL^{-1} in DMF at 25 °C.

^c Measured without filter.

observed at 1776–1777 cm^{-1} . These are attributed to the asymmetric and symmetric stretching vibrations of the imide carbonyl groups. The bands of C–N bond stretching and ring deformation appear at 1375–1376 cm^{-1} . Strong bands of absorption, which were characteristic of the new formed amide linkage, appeared at around 3426–3500 cm^{-1} . They were assigned to N–H stretching vibration. At 1670–1672 cm^{-1} , this can be attributed to stretching vibration of amide, and at 1541–1546 cm^{-1} , it is due to N–H bending vibration. The absorption band at around 3100 cm^{-1} was attributed to =CH aromatic linkage. A representative FT-IR spectrum for PAI8a is illustrated in Fig. 1. Some of the polymer's structures were also confirmed by ^1H NMR spectroscopy. Fig. 2 shows the ^1H NMR (400 MHz) spectrum of PAI8a. In the ^1H NMR spectrum of this polymer, the appearances of the N–H protons of amide groups at 10.31, 10.92, and 12.73 ppm, as three singlet peaks, indicate the presence of amide groups in the polymer's structure. The resonance of aromatic protons appeared in the range of 7.26–8.52 ppm. Also, the proton of the chiral center appeared as doublet at 4.64–4.66 ppm.

Polymer solubility

The solubility of the obtained PAIs (8a–8d) was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the synthesized polymers were soluble in organic solvents such as DMF, DMAc, DMSO, N-methylpyrrolidone, m-cresol, pyridine, and in H_2SO_4 at RT. They are insoluble in solvents such as methanol, ethanol, chloroform, methylene chloride, ethyl acetate, diethyl ether, and water.

Thermal analysis of polymers

The thermal stability of the copolymers was characterized by TGA carried out in N_2 at a heating rate of 20 $^\circ\text{C min}^{-1}$, and their corresponding weight loss temperatures of 5% and 10% ($T_{d5\%}$ and $T_{d10\%}$) were all determined from original TGA curves. All the aromatic PAIs exhibited good thermal stability with insignificant weight loss up to 360 $^\circ\text{C}$ in nitrogen. The $T_{d5\%}$ and $T_{d10\%}$ values of the PAIs stayed within the ranges of 365–389 and 388–410 $^\circ\text{C}$, respectively. The amount of carbonized residue (char yield) (CR) of these polymers in nitrogen

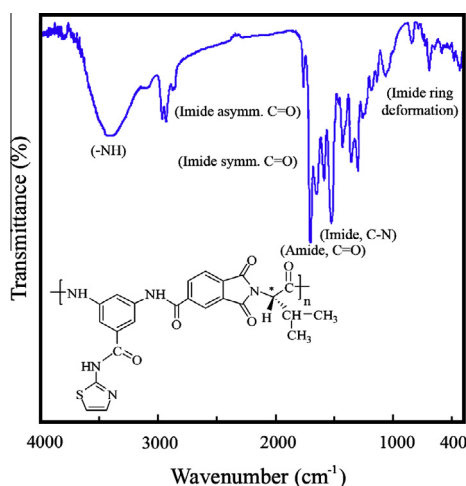


Fig. 1 FT-IR spectrum of poly(amide-imide) 8a.

atmosphere was up to 43% at 800 $^\circ\text{C}$. The high char yields of these polymers can be ascribed to their high aromatic content. Obviously, the data from thermal analysis showed that these PAIs have a fairly high thermal stability. Typical TGA curves of representative PAIs 8a and 8b are shown in Fig. 3.

Limited oxygen index-self extinguishing polymer

The limiting oxygen index (LOI) is a measure of the percentage of oxygen to be present to support the combustion of the material. The LOI value can be used to evaluate the flame-retardancy of polymers. The percentage of oxygen in the air is around 21%. It is clear that all materials with an LOI lower than this level will burn easily, while those with a higher LOI will tend not to burn. Theoretically, according to Van Krevelen equation [30], CR can also be used as a criterion for evaluating LOI of polymers.

$$LOI = \frac{(17.5 + 0.4CR)}{100}$$

PAI 8a and 8b had LOI value 36.3 and 35.1, respectively, which were calculated from their CR. According to this equation, a higher CR will enhance flame retardance. On the basis of the LOI values, such PAIs can be used as self-extinguishing polymers.

According to Johnson equation [31], there is also an interesting relationship between the LOI and heat of combustion.

$$LOI = \frac{8000}{\Delta H_{comb}}$$

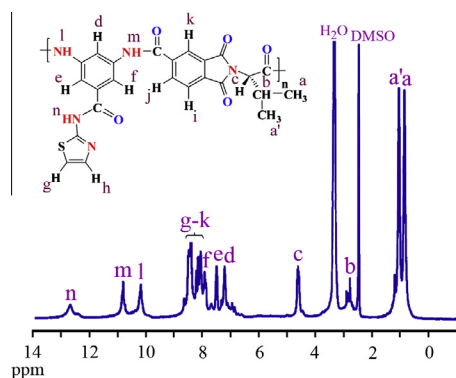


Fig. 2 ^1H NMR (400 MHz) spectrum of PAI8a in DMSO-d_6 at RT.

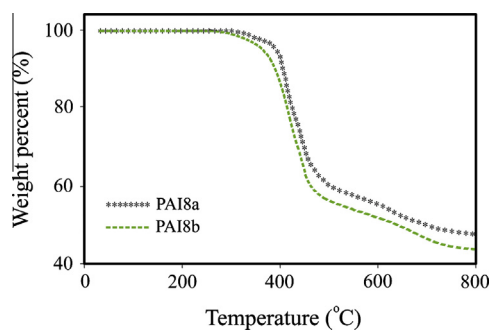


Fig. 3 TGA curves of PAI8a and PAI8b (in nitrogen at a heating rate of 10 $^\circ\text{C min}^{-1}$).

where ΔH_{comb} is the specific heat of combustion in J/g. So, in the case of these polymers (PAI8a and PAI8b), ΔH_{comb} is 22.0 and 22.7, respectively.

Film characteristics and optical properties

All the prepared PAIs are lightly colored, and they were also subjected to UV–vis spectrum. From the spectral results in Table 2, it has been confirmed that the presence of alkyl groups in the polymer backbone has eliminated the electronic polarization by breaking up the extended conjugation along the chain, which results in color. Apart from this, the incorporation of a bulky thiazole unit has also inhibited the chain-chain packing via the increased entropy mechanism. However, the small variations observed in the cutoff wavelength may be due to the nature of diamine and anhydride moieties present in the polymer backbone. These polymers, exhibiting strong UV–vis absorption bands at 270–271 nm in DMAc solution, are peculiar to the combinations of $n-\pi^*$ and $\pi-\pi^*$ transitions. They result from the conjugated thiazole group. On the other hand, to prepare a crack-free and homogeneous thin film, solutions of the polymers were made by dissolving 0.50 g of the samples in 5 mL of DMAc. These solutions were poured into an 8 cm glass Petri dish, which was heated under vacuum at 90 °C in an oven overnight, 100 °C for 3 h, 120 °C for 2 h, and 150 °C for 1 h to evaporate the solvent slowly. Being soaked in distilled water, the flexible and transparent thin film with low color intensity was self-stripped off from the glass surface. The obtained films were then used to investigate the optical properties of the PAIs. The plateau region of the light transmittance in the UV–vis spectra was extended to about 500 nm, indicating the high degree of the films transparency [32]. Moreover, the λ_0 values (absorption edge or cutoff wavelength) of the resulting PAIs were found to be in the range of 433–434 nm. Generally, the results obtained clearly show that the prepared thin films have low color intensity and a high level of optical transparency in the UV–vis light region. Table 2 lists the characteristics of the resulting films and the values of absorption edge. Furthermore, Fig. 4 shows molar absorptivity spectrum of representative PAI8a solution (a) and UV–vis transmission spectrum of the same polymer film (b).

XRD patterns and microstructure of the PAIs

The crystallinity of the PAIs was examined by XRD. X-ray diffractograms are given in Fig. 5. In general, the diffraction patterns were broad, indicating that most of these PAIs were amorphous. The amorphous character is due to the presence of $-\text{CO}-\text{NH}-$, $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{CH}_3-$, and imide

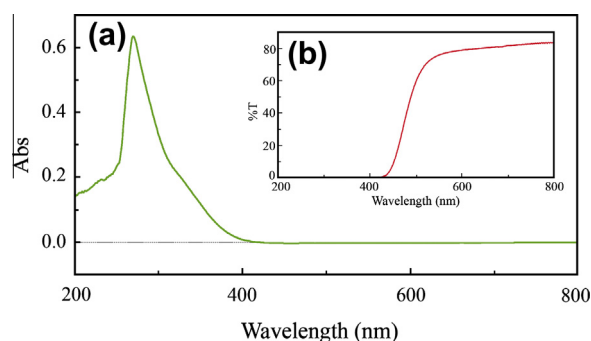


Fig. 4 Molar absorptivity spectrum of polymer PAI8a solution (a). UV–vis transmission spectrum of the same polymer film (b).

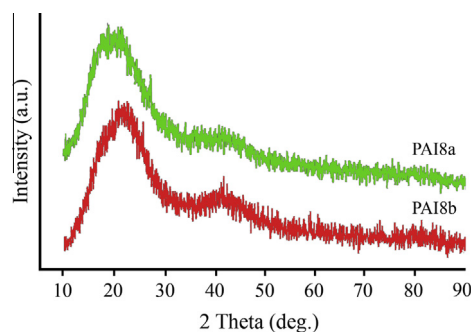


Fig. 5 XRD patterns of PAIs 8a and 8b.

groups in the chain, which prevents the chain–chain interaction, leading to amorphous morphology. Morphological characterization of PAIs was studied by FE-SEM. The microstructure of the PAIs is presented in Fig. 6a–d. As can be seen from these images, the average diameter of polymeric particles is in the range of 38–53 nm. They are distributed uniformly and randomly in a filamentary morphology.

It is well known that ultrasonic irradiation is a well-established method for particle size reduction in dispersions and emulsions as well as generation and application of nano-size materials, because of the potential in the deagglomeration and the reduction of primaries. As most nanomaterials are still fairly expensive, this aspect is of high importance for the commercialization of product formulations containing nanomaterials [33]. Herein, powders of polymers have been subjected to irradiation with high-intensity ultrasound for one hour while being suspended in ethanol. The homogeneous suspension was placed in a 60 °C oven overnight to evaporate most of the solvent. Then, the semidried polymer powder was further dried in vacuo at 80 °C for 8 h. The resulting images from

Table 2 Film characteristics and optical behavior of PAIs.

Polymer	$\lambda_{abs,max}$ (nm) ^a	Film characteristics ^b	λ_0 (nm) ^c
8a	273	Transparent, Flexible, Yellow	430
8b	273	Transparent, Slightly brittle, Yellow	430
8c	271	Transparent, Flexible, Yellow	432
8d	272	Transparent, Slightly brittle, Yellow	432

^a From UV–vis absorption spectra measured in DMAc solution (0.02 mg/mL) at room temperature.

^b Film thickness was about 40 μm .

^c The cutoff wavelengths (λ_0) from the transmission UV–vis absorption spectra of polymer films. Cutoff wavelength is defined as the point at which the light transmittance from the prepared thin films becomes less than 1%.

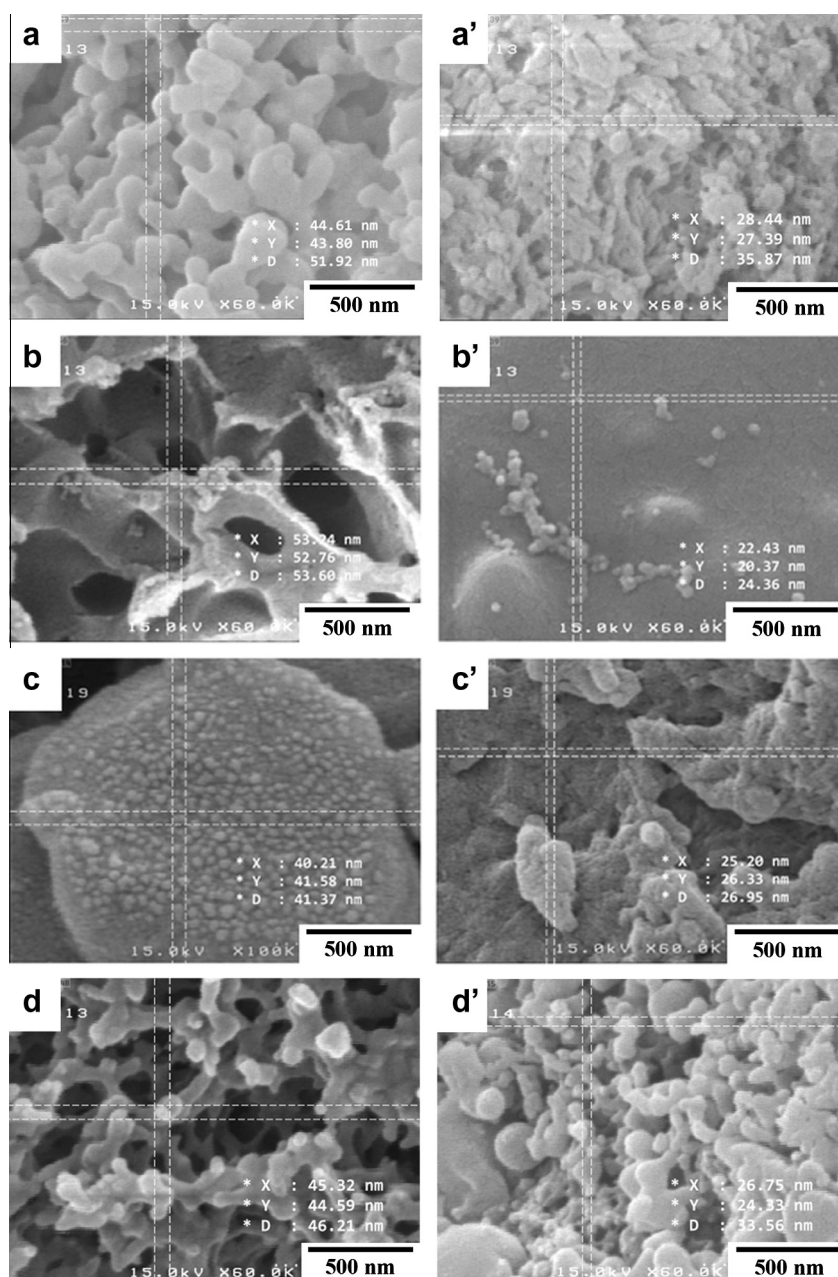


Fig. 6 FE-SEM micrographs of PAIs before ultrasonication (a-d) and after ultrasonication of suspended polymer in ethanol (a'-d').

FE-SEM confirmed that after ultrasonic irradiation, the size of polymeric nanoparticles was decreased (22–31 nm) and the morphology of them was also changed (Fig. 6a'-d').

Conclusions

The applications of microwave irradiation in the polycondensation reaction of an aromatic thiazole ring-containing diamine with several diacids that contained flexible amino acid linkages in the molten TBAB salt have been investigated. As has been demonstrated, the coupling of microwave technology and molten salt conditions creates a clean, selective, and efficient methodology for performing certain organic reactions with substantial improvements in terms of mild conditions and simplicity of operating procedures. The ob-

tained polymers showed a superior solubility in a variety of common organic solvents. The surface of the thin films obtained from these polymers is smooth, without pinholes. Accordingly, all the polymeric low-colored thin films were significantly flexible and showed a high optical transparency in the UV-vis light region. Most of these PAIs have a high thermal stability with initial decomposition temperatures being in the range of 365–389 °C. These properties suggesting that the obtained polymers can be applied as new materials for engineering plastics.

Conflict of interest

The authors have declared no conflict of interest.

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