

ORIGINAL ARTICLE

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



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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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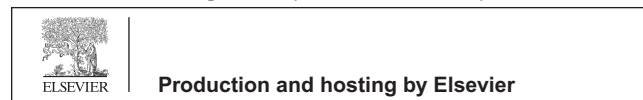
Introduction

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

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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

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