

*a* = microwave radiation for 15 min.

## ORGANIC CHEMISTRY | RESEARCH ARTICLE

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# Microwave-assisted solvent-free synthesis of new polyimine

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**Abstract:** Microwave irradiation method indicated points of interest for the produced polymer that contrasted with that prepared by a routine strategy, where it can offer a polymer in brief time, high yield, higher molecular weight because of the prevention action of the chain exchange, more pure compounds, and all the more thermally stable polymers, instead of the conventional technique. Benzil and p-phenylenediamine were built into the main chain to prepare a new polymer named polyimine, utilizing microwave route as a part of 95% yield, and characterized it by Fourier transform infrared (FT-IR), UV-visible, and nuclear magnetic resonance (NMR) techniques. The thermal properties of the new polymer were evaluated by thermal gravity analysis (TGA).

**Subjects:** Applied & Industrial Chemistry; Chemical Spectroscopy; Materials Chemistry; Organic Chemistry

**Keywords:** microwave NMR; polymer; FT-IR

### 1. Introduction

Microwave-assisted organic synthesis has been recognized as one of the most interesting areas of current chemical research (Caddick, 1995; Lidström, Tierney, Wathey, & Westman, 2001; Mallakpour & Rafiee, 2008; Matloobi & Kappe, 2007; Perreux & Loupy, 2001). Microwave heating has developed as a capable method to promote a variety of chemical reactions, offering reduced contamination, minimal effort, and high yields together with effortlessness in processing and handling (Adam, 2003; Karah, 2002; Lerestif et al., 1997; Loupy, 2004; Varma, 2002; Varma, Dahiya, & Kumar, 1997). The utilization of microwave irradiation to organic synthesis has been the focus of extensive consideration lately and is turning into an undeniably well-known innovation (Al-Hazimi, El-Faham, Ghazzali, & Al-Farhan, 2012; Ghazzali, El-Faham, Abdel-Megeed, & Al-Farhan, 2012; Kidwai, 2001; Raval & Desai, 2005, 2009; Raval, Desai, & Desai, 2006; Raval, Desai, Desai, & Desai, 2008; Raval,



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Furkan Kamil received her bachelor's degree of Optoelectronics Engineering in 2013 from the University of Technology/Baghdad-Iraq and is currently pursuing her master's degree in Optoelectronics in the University of Technology in Baghdad under the supervision of Kadhim Abed Hubiter and Ahmed Al-Amiry. Her research focuses on the preparation and characterization of polymeric solar cell complemented with efficiency enhancement by laser.

### PUBLIC INTEREST STATEMENT

Polymers are large molecules composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. A polymer solar cell is a type of flexible solar cell made with polymers, large molecules with repeating structural units, that produce electricity from sunlight by the photovoltaic effect. Polymer solar cells include organic solar cells. They are one type of thin film solar cell, while others include the more stable amorphous silicon solar cell.

Patel, Patel, Patel, & Desai, 2009). As of late, there has been developing interest for applying microwave irradiation to polymer synthesis (Imai, Nemoto, Watanabe, & Kakimoto, 1996; Jullien & Valot, 1985; Liu, Sun, Xie, & Scola, 1998; Silinski, Kuzmycz, & Gourdenne, 1987) as it can quicken numerous syntheses, providing selective activation with short start-up stage, and can permit quick optimization of reactions. In light of these discoveries, we attempt to depict a straightforward strategy for the synthesis of polyimine polymer utilizing a microwave technique with the point of acquiring a more steady polymer with exceptional properties. The chemical structure of the newly synthesized polymer was confirmed by spectroscopic techniques (FT-IR, NMR, and UV-vis). The thermal stability of all synthesized polymer was also investigated.

## 2. Experimental

### 2.1. Chemicals

All chemicals utilized as a part of this study were of reagent grade. Analytical reagents (AR) were supplied by either Sigma-Aldrich or Fluka, and utilized without purification.

### 2.2. Instrumentation

The FT-IR spectra were recorded in the (4,000–400  $\text{cm}^{-1}$ ) range on potassium bromide discs utilizing a Shimadzu FT-IR 8400S spectrophotometer. Proton NMR spectra were recorded on Burker DMX- 500 NMR spectrophotometer on 300 MHz, with TMS as the internal standard and DMSO as the solvent. The UV-visible spectra were measured using a Shimadzu UV-vis. 1650 spectrophotometer in the range (200–1,000 nm). The reactions were made using Microwave Oven Russell Hobbs 800 Watt.

### 2.3. Synthesis of the polymer

The synthesis of polyimine was achieved by microwave irradiation technique. Benzil (0.01 mol, 2.1 g) was thoroughly grounded with appropriate solid p-phenylene diamine (0.01 mol, 1.08 g) in a dry mortar with the help of a pestle to make an easy flowing powder. This material was subsequently taken in a dry conical flask. The mixture was irradiated under microwave for 15 min at 800 W, 2,450 MHz with constant shaking. After the completion of the reaction, the contents of the flask were cooled down until the liquid solidified. It was then inverted and the walls were scraped out to give the polymer.

## 3. Result and discussion

The condensation of benzil with p-phenylenediamine in a solvent-free reaction was carried out in a domestic microwave oven. The reaction sequence for the synthesis of the new polyimine polymer derived from benzil and p-phenylenediamine is outlined in Scheme 1.

### 3.1. Spectra characterization of the new polymer

The FT-IR spectrum (Figure 1) of the new polymer showed in general disappearing (N-H) and (C=O) bands (for the monomers), and a new appearing band for (C=N) stretching at (1,672  $\text{cm}^{-1}$ ). The  $^1\text{H-NMR}$  spectrum in DMSO exhibited multiple bands at  $\delta$  6.85–7.83 (m, 1H, aromatic ring) (Figure 2). The ultra-violet spectrum (Figure 3) of the synthesized polymer showed two absorption bands, the position of

Scheme 1. Synthesis of polyimine.

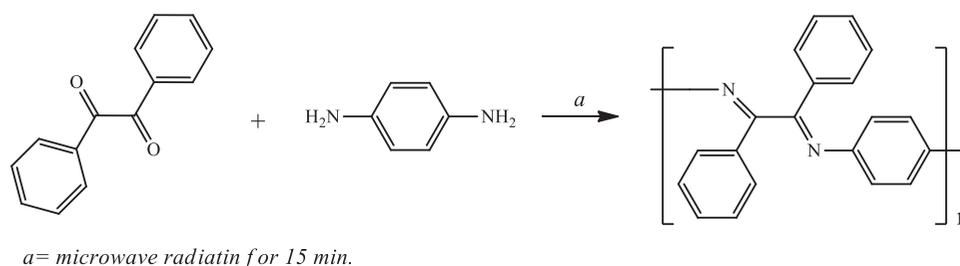


Figure 1. The FT-IR spectrum of the newly synthesized polymer.

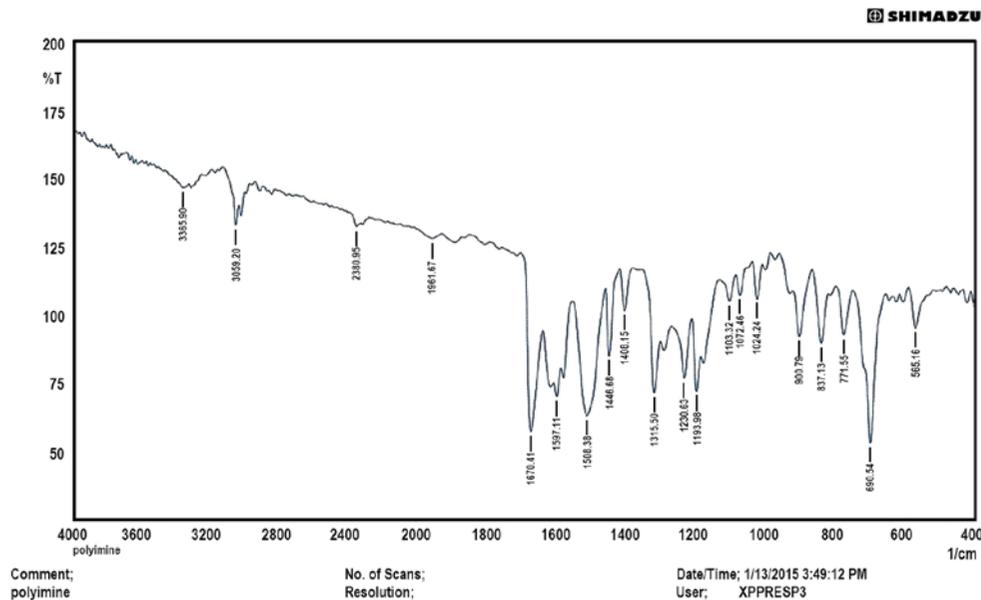
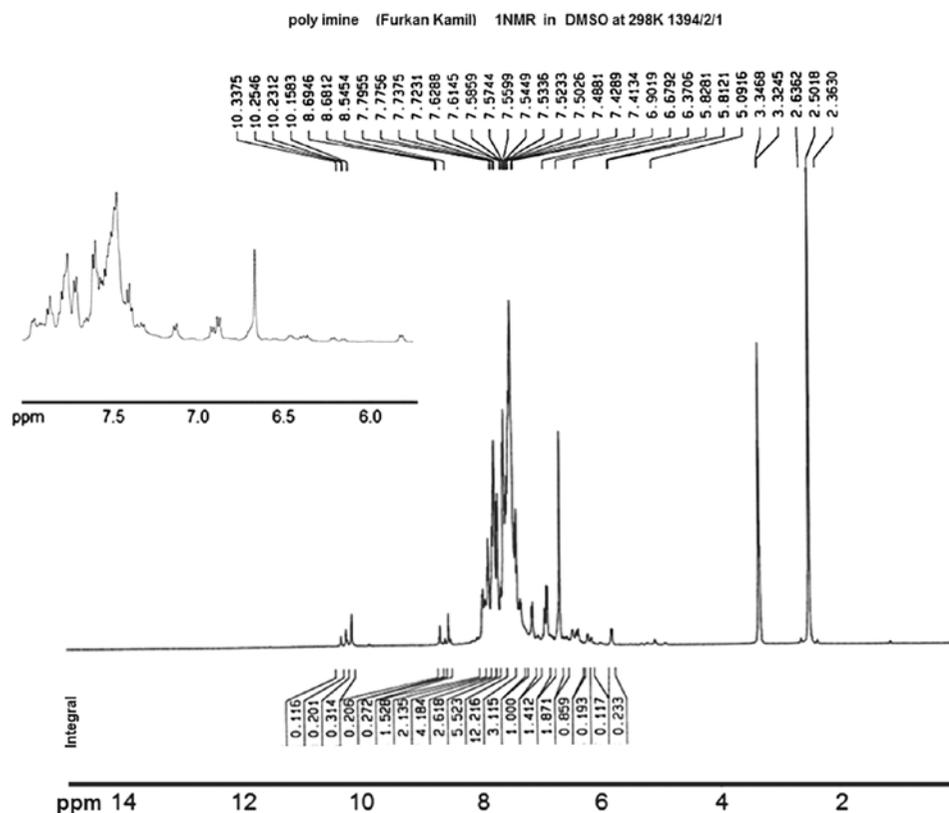


Figure 2. The NMR spectrum of the newly synthesized polymer.



the first band at 266 nm ( $37,593.98\text{ cm}^{-1}$ ), which represents the ( $\pi\rightarrow\pi^*$ ) transition, while the second band (which has higher intensity than the first band due to conjugated system) appeared at 331 nm ( $30,211.48\text{ cm}^{-1}$ ) and represents the ( $n\rightarrow\pi^*$ ) transition.

Figure 3. The UV-vis spectrum of the newly synthesized polymer.

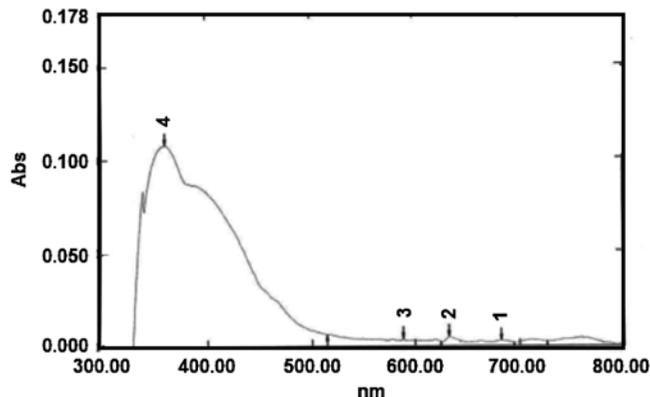
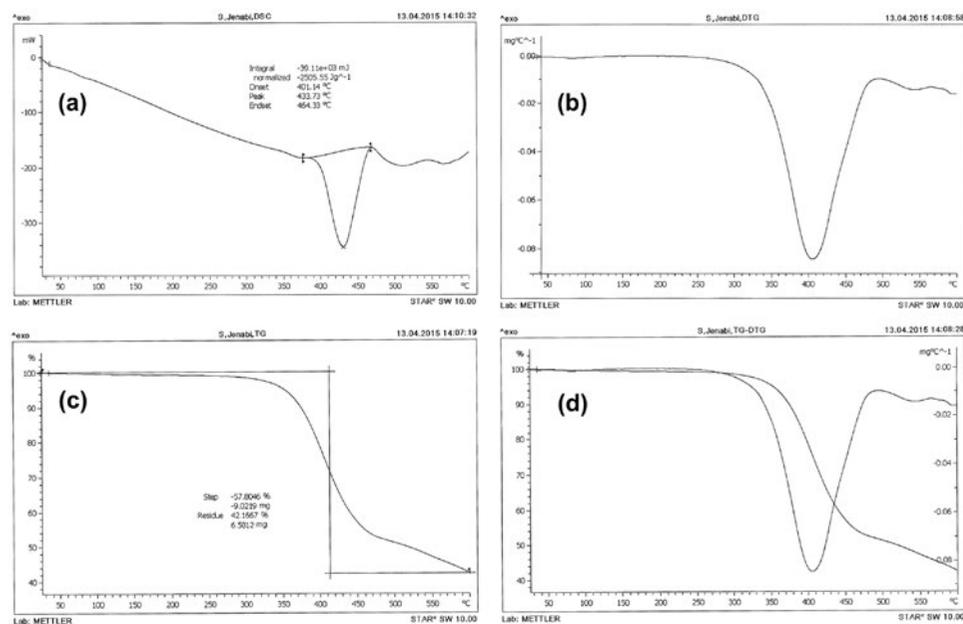


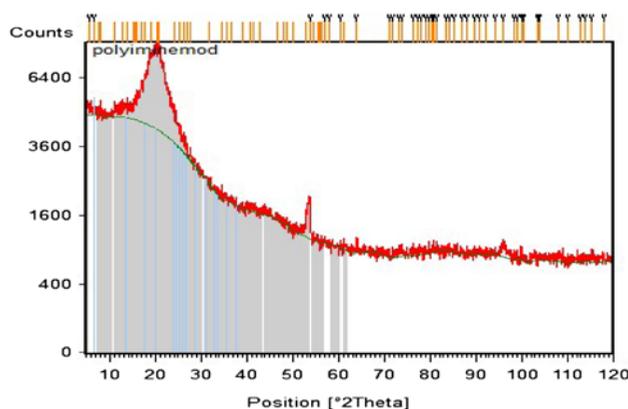
Figure 4. The thermogravimetric analysis (TGA) of the newly synthesized polymer.



### 3.2. Thermogravimetric analysis (TGA) of polyimine

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate) or as a function of time (with constant temperature and/or constant mass loss) (Coats & Redfern, 1963). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena, including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g. oxidation or reduction) (Coats & Redfern, 1963). TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are characterization of materials by analyzing characteristic decomposition patterns, studies of degradation mechanisms and reaction kinetics, determination of organic content in a sample, and determination of inorganic content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. The thermal stability of the prepared polyimine can be evaluated by TGA. The TG curves of polyimine at heating rate of  $5^{\circ}\text{C min}^{-1}$  are shown in Figure 4 (a-d). The TG curves indicate that the solvent has been successfully eliminated from polyimine because there is no weight loss below  $100^{\circ}\text{C}$ . It can be clearly seen in Figure 4 that the residual weight of polyimine

Figure 5. The XRD spectrum of the newly synthesized polymer.



thermal decomposition is higher than polyimine above 450°C. The increase in the weight residues above 450°C illustrates increases in thermal stability. The improvement of the thermal stability of the prepared polyimine can be based on the fact that this polymer has inherently good thermal stability and also due to the strong chemical bonding that exists between the monomers of polyimine. Figure 4 (a–d) shows the TGA results generated for polyimine. The plot shows the percent mass as a function of sample temperature for polyimine. The TGA results show that polyimine polymer undergoes thermal degradation beginning at 450°C and with a total mass loss of 50.0%. There is a small amount of inert residue remaining (50.0%).

### 3.3. X-ray characterization of the newly synthesized polymer

The prepared polymer was characterized by XRD. Figure 5 shows the XRD patterns of polyimine. As is clearly seen in Figure 5, there is a peak in the diffractogram of polyimine as the non-Gaussian distribution pattern that reveals a semi-crystalline structure polymer. This peak was also depicted in all of the diffractograms of polyimine polymer.

## 4. Conclusions

Synthesis of a new polymer namely polyimine was done in this paper. The thermal properties of the new type of polyimines based on Benzil and p-phenylene diamine were evaluated by the thermogravimetric analysis (TGA). The characterization of the polymer was done based on FT-IR, NMR, UV-vis, and XRD techniques.

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