Thermochimica Acta 518 (2011) 72–81

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Oxidative synthesis of a novel polyphenol having pendant Schiff base group: Synthesis, characterization, non-isothermal decomposition kinetics

Deniz Dilek[a], Fatih Doğan[a], Ali Bilici[b,*], İsmet Kaya[c]

[a] Faculty of Education, Secondary Science and Mathematics Education, Canakkale Onsekiz Mart University, 17100 Canakkale, Turkey
[b] Control Laboratory of Agricultural and Forestry Ministry, 34153 İstanbul, Turkey
[c] Department of Chemistry, Faculty of Science and Arts, Canakkale Onsekiz Mart University, Canakkale, Turkey

ARTICLE INFO

Article history:
Received 16 November 2010
Received in revised form 5 February 2011
Accepted 9 February 2011
Available online 16 February 2011

Keywords:
Oxidative polymerization
Thermal analysis
Non-isothermal decomposition kinetics

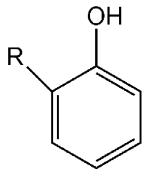
ABSTRACT

In here, the facile synthesis and thermal characterization of a novel polyphenol containing Schiff base pendant group, poly(4-{[(4-hydroxyphenyl)imino]methyl}benzene-1,2,3-triol) [PHPIMB], are reported. UV–vis, FT-IR, ^{1}H NMR, ^{13}C NMR, GPC, TG/DTG-DTA, CV (cyclic voltammetry) and solid state conductivity measurements were utilized to characterize the obtained monomer and polymer. The spectral analyses results showed that PHPIMB was composed of polyphenol main chains containing Schiff base pendant side groups. Thermal properties of the polymer were investigated by thermogravimetric analyses under a nitrogen atmosphere. Five methods were used to study the thermal decomposition of PHPIMB at different heating rate and the results obtained by using all the kinetic methods were compared with each other. The thermal decomposition of PHPIMB was found to be a simple process composed of three stages. These investigated methods were those of Flynn–Wall–Ozawa (FWO), Tang, Kissinger–Akahira–Sunose (KAS), Friedman and Kissinger methods.

1. Introduction

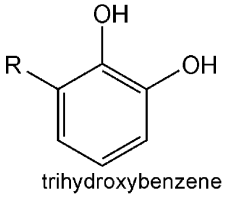
More recently, many studies have been reported on oxidative polymerization (OP) of phenols. OP is an alternative process for the preparation of phenolic resins without using formaldehyde [1]. This method has several advantages: no use of toxic formaldehyde, mild reaction conditions and facile procedure [2,3]. It has also been reported that the polyphenols obtained by OP consist of a mixture of phenylene and oxyphenylene units, different from the composition of conventional phenol resins [4,5]. Polymerization of various kinds of phenol monomers has been reported up till know. Some of them are phenols bearing Schiff base in their structures. OP of monohydroxy, dihydroxy phenols having Schiff base units as side group has been widely studied in acidic and alkaline medium [6–12]. Phenol monomers were also catalytically polymerized in presence of enzymes, metal complexes and metal salts [5,13,14].

monohydroxybenzene



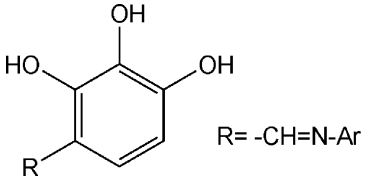
Refs. [6–10]

dihydroxybenzene



Refs. [11,12]

trihydroxybenzene

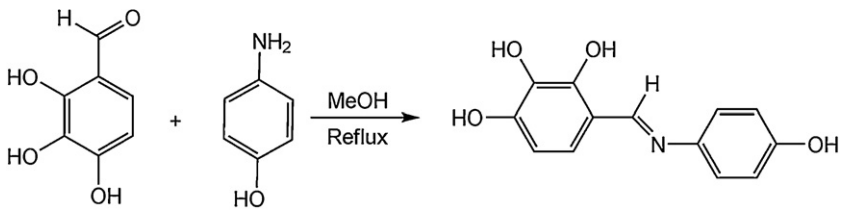


Ref. This study

However, to best of our knowledge, OP of trihydroxy substituted phenols having Schiff base units, has not been studied

* Corresponding author. Tel.: +90 212 663 39 61; fax: +90 212 663 42 96.
E-mail addresses: fatihdogan@comu.edu.tr (F. Doğan), alibilici66@hotmail.com (A. Bilici).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.02.009



Scheme 1. The synthetic procedure for preparation of HPIMB.

in alkaline medium, up till know. In this work, the synthesis and OP of a new Schiff base, HPIMB, were studied in alkaline medium to obtain a new functional polyphenol and non-isothermal methods were used to evaluate the thermal decomposition kinetics of resulting polymer. The resulting products were also characterized by means of cyclic voltammetry, conductivity measurements.

2. Materials and methods

2.1. Materials

2,3,4-trihydroxybenzaldehyde, *p*-aminophenol and solvents were supplied from Merck Chem. Co. (Germany) and they were used as received. Sodium hypo chloride (NaOCl) (30% aqueous solution) was supplied from Paksoy Chem. Co. (Turkey).

2.2. Synthesis of 4-{[(4-hydroxyphenyl)imino]methyl}benzene-1,2,3-triol (HPIMB)

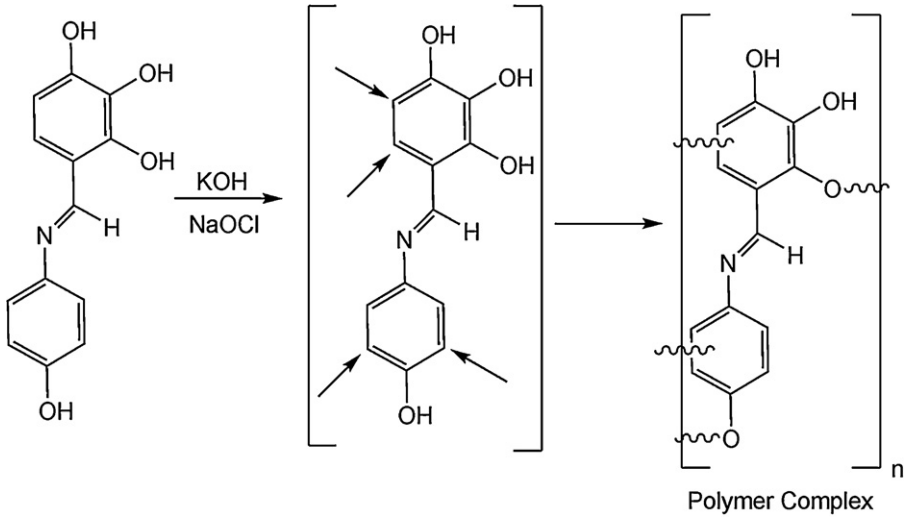
The Schiff base monomer, abbreviated as HPIMB, was synthesized by the condensation reaction of 2,3,4-trihydroxybenzaldehyde with the *p*-aminophenol. Reaction was performed as follow: *p*-aminophenol (1 mmol) was placed into a 250-mL three-necked round bottom flask which was fitted with condenser, thermometer, and magnetic stirrer, and 30 mL methanol was added into the flask as a solvent. A solution of aldehyde (1 mmol) in 20 mL methanol was added into the flask. Reaction was maintained for 3 h under reflux (Scheme 1). The precipitated Schiff base was filtered, recrystallized from methanol, and dried in vacuum desiccators.

2.3. Synthesis of poly(4-{[(4-hydroxyphenyl)imino]methyl}benzene-1,2,3-triol)

The synthesized monomer was converted to corresponding polymer derivative in an aqueous alkaline medium as described in elsewhere [10]. A solution of NaOCl (30%, in water) was used as oxidant. The synthetic pathway is given in Scheme 2.

2.4. Characterization techniques

The solubility tests of monomer and polymer were carried out by using sample of 1 mg and solvent of 1 mL at 25 °C. Electronic absorption spectra were measured using a Perkin–Elmer Lambda 25 spectrometer. The infrared spectra were obtained on Perkin Elmer Spectrum One FT-IR system using universal ATR sampling accessory within the wavelengths of 4000–550 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) were recorded at room temperature in deuterated DMSO. TMS was used as internal standard. SEC analyses were performed at 30 °C using DMF/MeOH (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min. The instrument (Shimadzu 10AVp series HPLC–SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, Mp, between 162 and 19,880) using GPC software for the determination of the molecular weight (M_n), weight–average molecular weight (M_w) and polydispersity index (PDI) of the polymer sample. Macherey–Nagel GmbH & Co. (100 Å and 7.7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns were used for SEC analyses. Conductivity measurements were performed on a Keithley 2400 electrometer. Samples were pressed on a hydraulic press developing to 1700 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure in a desiccator. Electrochemical properties of monomer and polymer were determined by using a CH instrument 660B Electrochemical Analyzer in 0.1 mol L^{-1} tetrabutylamonium



Scheme 2. The synthetic procedure for preparation of PHPIMB.