Polymer Degradation and Stability 112 (2015) 27–34

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Enzymatic synthesis of a polymeric antioxidant for efficient stabilization of polypropylene

Ke Zheng [a, b], Hang Tang [c], Qiumei Chen [c], Lei Zhang [b, c], Yufeng Wu [c], Yuanchen Cui [a, *]

[a] Key Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475000, People's Republic of China
[b] Institute of Chemistry and Biology, Henan University, Kaifeng 475000, People's Republic of China
[c] College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475000, People's Republic of China

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form
6 December 2014
Accepted 10 December 2014
Available online 19 December 2014

Keywords:
Enzyme-catalyzed polymerization
Poly(pyrogallic acid)
Phenolic antioxidant
Protection efficacy
Polypropylene
Thermal stability

ABSTRACT

Enzyme-catalyzed polymerization of pyrogallic acid is reported as a new method for preparing effective antioxidant for polypropylene (PP). Besides, this polymerization was performed in aqueous micelle, an environmentally benign system, using horseradish peroxidase (HRP) as catalyst. Poly(pyrogallic acid) exhibits better thermal stability than pyrogallic acid. Data from radical scavenging and ferric reducing antioxidant potential assay suggest that poly(pyrogallic acid) has excellent radical scavenging capacity and ferric ion reducing ability. Characterization of PP by thermal methods tests indicate that poly(-pyrogallic acid) possesses better antioxidant ability than pyrogallic acid and many commercial antioxidants. Thus, poly(pyrogallic acid) is proposed as a high efficiency, eco-friendly, and easily accessible antioxidant to inhibit thermo-oxidative degradation of PP.

1. Introduction

Enzyme-catalyzed polymerization of phenol has drawn much attention, since it involves mild reaction conditions and facile procedures [1,2]. By utilizing enzyme catalysis, researchers have successfully synthesized a new class of polyphenols which can hardly be obtained from conventional chemical methods [3–5]. Enzymatic polymerization of phenol derivatives can provide phenol polymers with good thermal stability. Besides, the solubility and structure of the pre-designed polymers can be readily controlled by properly adjusting the reaction conditions [6,7]. Thus enzymatic polymerization of phenol derivatives is of particular significance for preparing polyphenols [8,9].

Usually, enzymatic polymerization of phenols is performed in aqueous organic solvents using HRP as enzymatic catalyst since it was reported to maintain its activity even in a mixture of buffer and water-miscible organic solvent [10,11]. The above reaction system, unfortunately, often need to use a large amount of organic solvents, because the enzymatic polymerization of phenol in pure water only provides target polymers in low yield [12]. As a result, it is disadvantageous from the standpoint of being an environmentally benign process for preparing phenols polymer. The mentioned disadvantage could be eliminated when poly(ethylene glycol) or cyclodextrins are adopted as additives to conduct the enzymatic polymerization of phenol in aqueous system [13,14].

This strategy, however, can not provide pure polymers owing to the presence of additives. In addition, polymerization of phenol can be carried out in ionic liquids; nevertheless, the system is too expensive [15,16]. Recently, we found that enzymatic phenol polymerization could be performed efficiently with tiny amount of HRP in aqueous micelle system, and the target polymer can be obtained with high purity after fully flushing with deionized water [17,18]. Thus, aqueous micelle system is proposed as a novel eco-friendly system to the synthesis of phenolic polymer and may be widely used in industry fields.

It is known that hindered phenolics are widely used as primary antioxidants for PP [19]. Recently, however, it is reported that hindered phenols with low molecular weight could easily departed from host materials by migration and evaporation, which decreases the efficiency of antioxidants [20,21]. Of various methods for minimize the physical loss of antioxidants, increase the molecular weight of antioxidants has been widely applied in industries [22,23]. So far, many antioxidants with high molecular weight have been synthesized by traditional chemical methods [24]. However,

* Corresponding author. Tel.: +86 0371 23881589.
E-mail address: yuanchencui@126.com (Y. Cui).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.12.009
0141-3910/

the concern over the formation of complex products and the harsh conditions used by these methods may limit the appeal of such antioxidants prepared through the non-enzymatic route. In this respect, synthesis of polymeric phenols based on enzyme-catalyzed polymerization may be of particular significance, which gives a novel easily accessible and eco-friendly approach to yield antioxidant of polymer materials.

In the present paper, we report a facile access to a novel polymer of pyrogallic acid, poly(pyrogallic acid), via an eco-friendly and easily accessible horseradish peroxidase (HRP)/H_2O_2-catalyzed oxidation process and evaluate the radical scavenging capacity of this new phenolic polymer. In addition, the potent stabilizing effects of poly(pyrogallic acid) on PP were disclosed.

2. Materials and methods

2.1. Materials

HRP (activity = 200 U/mg) was purchased from Shanghai Guoyuan Biotechnology Company Limited (Shanghai, China) and used without further purification. Sodium dodecyl sulfate (SDS), pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) (Irganox 1010), 3, 5-ditertbutyl-4-hydroxybenzenepropanoic acid thiodi-2, 1-ethanediyl ester (Chinox 1035), octadecyl 3-(3, 5-di-tert-butyl-4-hydroxyphenyl) propionate (Irganox 1076), butylated hydroxyanisole (BHA) and 2, 6-di-tert-buty-4-methylphenol (BHT) were purchased from J&K Scientific Company Limited (Beijing, China). 2, 2-Diphenyl-1-picryhydrazyl (DPPH) and 2, 2′-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) were obtained from TCI Shanghai (Shanghai, China). 2, 4, 6-Tripyridyl-s-triazine (denoted as TPTZ) was purchased from Energy Chemical Beijing (Beijing, China). The unstabilized PP powder was kindly donated by Chinese Sinopec Zhongyuan Petroleum Chemical Co., Ltd. Other reagents were purchased from various commercial suppliers and were used as received.

2.2. Analytical methods

The size of the aqueous micelle under investigation was measured by dynamic light scattering (Letasizer Nano ZS90, Malvern Instrument of England). The concentration of pyrogallic acid during the enzymatic polymerization was analyzed by high-performance liquid chromatograph (HPLC; Agilent 1100) equipped with a C18-reverse phase column (2.1 mm × 150 mm, 5 μm). The mixture of acetonitrile, distilled water and acetic acid with a volume ratio of 45: 55: 0.1 was used as the mobile phase (flow rate 0.4 mL/min); and pyrogallic acid was measured at 267 nm with an ultraviolet absorbance detector. Infrared (IR) spectra were recorded with VERTEX 70 Fourier transform infrared spectrometer (FT-IR; BRUKER Company, Germany). Nuclear magnetic resonance (^{1}H NMR) spectra were measured with an AVANCE 400 MHz spectrometer (Bruker Company, Germany). The molecular weight of as-prepared pyrogallic acid polymer was estimated by gel permeation chromatography (GPC; Water 515 pump and Waters 2414 refractive index detector) with dimethylformamide (DMF) as the eluent (flow rate 1.0 mL/min). The calibration curves for GPC analysis were obtained using polystyrene as the standard. Thermogravimetric (TG) analysis under air atmosphere was performed with a TGA/SDTA851e instrument (Mettler-Toledo Company, Switzerland) at a heating rate of 10 °C/min. The absorption spectrum of sample was determined with a 723N-visible spectrophotometer (Chengguang Instruments Company Ltd.; Shanghai, China). Onset Oxidation Temperature (OOT) of PP was performed by differential scanning calorimeter (Mettler-Toledo Company, Switzerland) in air atmosphere at the flow of 50 mL/min at a heating rate of 10 °C/min. OOT was defined as the temperature when the heat flow started to change abruptly after melting peak. Oxidation Induction Time (OIT) was measured using differential scanning calorimeter according to the standard method (ISO 11357-6: 2002). First, the sample was held at 25 °C for 5 min under a nitrogen flow of 50 mL/min. Then the sample was heated to 210 °C at a rate of 20 °C/min, and held at 5 min for equilibration, still under a nitrogen flow rate of 50 mL/min. After that the gas was switched to oxygen with the flow rate of 50 mL/min. The oxidation of the sample was observed as a sharp increase in heat flow due to the exothermic nature of the oxidation reaction. Melt flow index (MFI) was determined with an extrusion plastometer (Jingjian Co., Ltd., Chengde, China) according to ISO-1133 standard at 230 °C with 2.16 kg load [25].

2.3. Enzymatic polymerization of pyrogallic acid in aqueous micelle system

50 mL of buffer was placed into a flask, and then 0.1 g of surfactant (SDS) and 0.63 g of pyrogallic acid were added into the flask and dissolved. Into resultant mixed solution was added 1 mg of HRP, followed by dripping of 0.25 mL of aqueous solution of 5% hydrogen peroxide under mild magnetic stirring at an interval of 15 min (the total dripping times is 14, and it refers to a total amount of hydrogen peroxide is 3.5 mL) to allow the generation of precipitate. Upon completion of dripping of H_2O_2 solution, resultant precipitate was stirred for an additional 12 h, followed by addition of 10 g of NaCl. Resultant polymer precipitates were collected by vacuum filtration and washed with distilled water, followed by drying at 50 °C to give target product, a black powdery polymer.

2.4. Determination of antioxidant capacity

2.4.1. Antioxidant assay with DPPH free radical

The DPPH radical scavenging capacity of poly(pyrogallic acid) was evaluated according to the method of Brand-Willias [26]. Briefly, a proper amount of DPPH free radical was dissolved in ethanol to provide a solution with a concentration of 120 μM. Into 5 mL of as-obtained DPPH free radical solution was added 5 mL of the ethanol solutions of to-be-tested samples. Then resultant mixed solutions were incubated at 37 °C for 30 min. Upon completion of incubation, the absorbance (A_x) of the mixed solutions at 515 nm was measured, and the absorbance (A_0) of a blank sample containing 5 mL of ethanol and 5 mL of DPPH radical solution was also measured under the same conditions. All the measurements were conducted in triplicate; and radical scavenging activity is calculated as: inhibition efficiency (%) = $[(A_0 - A_x)/A_0] \times 100\%$. Here A_0 is the absorbance of DPPH in ethanol, and A_x is the absorbance of the ethanol solution containing poly(pyrogallic acid) and DPPH. The antioxidant capacity is expressed as I_{C50}, and it is defined as the polymer concentration (in mg/L) at which the absorbance of DPPH free radical is inhibited by 50% [27,28].

2.4.2. Antioxidant assay with ABTS radical cation

Traditional ABTS assay was used in this study [29]. Briefly, a proper amount of the stock solution of 7 mM ABTS was mixed with a proper amount of 2.45 mM potassium persulfate solution and incubated at room temperature in the dark for 16 h to afford concentrated ABTS radical cation solution. As-obtained concentrated ABTS radical cation solution was then diluted with ethanol until an absorbance of 1.40 ± 0.02 was obtained at 734 nm. Then 5 mL of ethanol solution of poly(pyrogallic acid) with different concentrations was separately added to 5 mL of the diluted ABTS radical cation solution. After the mixture was placed in 30 °C water bath for 10 min, the absorbance (A_x) was measured; and the absorbance (A_0) of the blank sample containing 5 mL of ethanol and