Polymer 55 (2014) 1443–1451

Contents lists available at ScienceDirect

Polymer

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

Use of renewable resource vanillin for the preparation of benzoxazine resin and reactive monomeric surfactant containing oxazine ring

Amy Van, Kevin Chiou, Hatsuo Ishida*

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

ARTICLE INFO

Article history:
Received 12 November 2013
Received in revised form
22 January 2014
Accepted 26 January 2014
Available online 1 February 2014

Keywords:
Polybenzoxazine
Renewable resource
Vanilin

ABSTRACT

A renewable natural resource, vanillin, is used to synthesize polybenzoxazine with the expected desirable benzoxazine properties as well as a high char yield of 55.3%. The synthesized monomer provides an unused aldehyde group from vanillin. The aldehyde can be further reacted with other materials to enhance properties. As a model, the unused aldehyde is reacted with amine terminated poly(ethylene oxide) to form a surfactant which retains 1,3-benzoxazine's reactivity. The chemical structure of the synthesized monomers, surfactant and polymers are characterized by Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Thermal properties are also characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Miniemulsions with stability up to 2 weeks are created with the newly synthesized surfactant and polystyrene. Dynamic light scattering (DLS) indicates 627 nm as the average diameter of the emulsion droplets.

1. Introduction

Polybenzoxazine is a class of polymers that exhibits various desirable properties such as near-zero volume changes, low water absorption, high char yield, high glass transition temperature, high tensile strength, and excellent chemical and thermal stability [1]. As a high performance thermoset, polybenzoxazine was utilized as matrix material for composites containing cellulose [2–4], glass fibers [5], carbon fibers [6–15], silicate nanofillers [16–32], and carbon nanofillers [33–42].

Polybenzoxazine monomers, 1,3-benzoxazine, can be synthesized in a 1-pot method from phenolic derivative, primary amine, and formaldehyde [43]. The functional groups on reactants are not utilized, therefore they allow customization of monomer and polymer for specialized properties. If functional groups do not interfere with polybenzoxazine polymerization, then different polybenzoxazine's properties remain similar [1]. Monomeric 1,3-benzoxazine undergoes ring-opening polymerization in the temperature range of 150–220 °C. This temperature range can be altered by additives or functional groups on the phenol and amine moieties used. Various functional groups, such as hydroxyl [44], carboxyl [45], and thiol [44], can be used to catalyze the ring-opening reactions. While benzoxazine resins are often used as polymerized bulk material, the properties in monomer form lead to various uses for constructing secondary structures [46].

Due to the environmental policies becoming ever more stringent and financial incentives from industries increasing, various fields in material science have shifted toward incorporating natural renewable resources into their products. With its flexible monomer synthesis mechanism, polybenzoxazine is a good candidate for incorporating naturally produced products and reducing reliance on petroleum derivatives as starting material [47]. Polybenzoxazine has been synthesized from waste byproducts of other industries, such as cardanol from the cashew nut industry, levulinic acid from cellulose degradation [48–51] and glycerin from biodiesel production [52]. Use of natural renewable resources for benzoxazine synthesis has recently been reviewed [48].

Aside from government and industry incentives, natural renewable resources often contain reactive functional groups that remain after synthesis to provide additional function to the resulting material [53,54]. Thus, each benzoxazine monomer synthesized using natural material can be complex in its interaction to other material in applications such as blend [55,56], composite [2–5], and molecular structure [46]. One natural renewable source that is underutilized is lignin, which is a major waste byproduct from the paper manufacturing. Lignin is a natural biopolymer that can be found in wood, aquatic plants, grasses, and other plant substances [57,58]. Lignin can be found in many forms in nature as it is often an

* Corresponding author.
E-mail address: hxi3@cwru.edu (H. Ishida).

0032-3861/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2014.01.041

amorphous polymer consisting of phenylpropane monomers [58]. Reports on the use of lignin for polybenzoxazines as a blend component have been reported [59,60].

Vanillin contain one open ortho position adjacent to the hydroxyl group, which makes vanillin a candidate for 1,3-benzoxazine synthesis. Vanillin can be synthesized from lignin and other renewable sources [61–64]. Currently, vanillin is used predominantly in the food and beverage industry, as well as in perfumes and pharmaceuticals. Vanillin can be found naturally produced by vanilla plants, but the majority of vanillin used in industry is created through chemical synthesis [62]. In addition to synthesis from lignin, vanillin can also be biosynthesized from many other compounds such as eugenol, ferulic acid, and aromatic amino acids using fungi, bacteria, or other genetically engineered microorganisms [62]. Vanillin is of great interest as a natural renewable reactant for benzoxazine chemistry, because vanillin contains an aldehyde group. The aldehyde is not consumed during synthesis. This aldehyde can be further used to react with other chemical groups or provide function to the benzoxazine monomer.

1,3-Benzoxazine groups are hydrophobic and do not dissolve into aqueous solutions, which makes benzoxazine groups useful as hydrophobic groups on a surfactant [65,66]. Previous benzoxazine surfactants were synthesized by incorporating a long hydrophilic polyetheramine tail as the amine during monomer synthesis. In the case of a benzoxazine monomer synthesized from natural renewable resources, such as vanillin, the monomers have functional groups to react to hydrophilic segments to form an amphiphilic molecule capable of supporting an emulsion. With benzoxazine groups acting as hydrophobic groups, stable emulsions can be produced.

An emulsion is a mixture of multiple immiscible fluids. In its simplest state, a two-phase system consisting of a dispersed phase and a continuous phase is stabilized by a surfactant. A surfactant ideally exists at the interphase of the two phases to reduce the interfacial tension and stabilize the regions. A miniemulsion of polystyrene in water was designed to take advantage of benzoxazine's affinity to polystyrene and polyetheramine's affinity to water to demonstrate a benzoxazine surfactant based on natural renewable resource's ability to perform its functions as a surfactant. Miniemulsion requires shearing with high shear process such as ultrasound to disperse the immiscible phases into quasi-stable droplets. Emulsion technique can be used for emulsion polymerization, drug delivery, food emulsion, and more [67].

2. Experimental

2.1. Materials

Vanillin (99%), aniline (99.5), and paraformaldehyde (95%) were used as received from Sigma Aldrich. Sodium hydroxide (97%), chloroform (99.5%), toluene (99.5), and anhydrous sodium sulfate (99.4%) were used as received from Fischer Scientific. Jeffamine M1000 (90%) and Epon 828 epoxy were courtesy from Huntsman and Momentive, respectively, and used as received.

2.2. Methods

2.2.1. Synthesis of 8-methoxy-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbaldehyde

8-Methoxy-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbaldehyde (hereinafter abbreviated as V-a) was synthesized from vanillin, aniline, and paraformaldehyde according to Scheme 1. Vanillin (5.70 g, 0.037 mol), aniline (3.49 g, 0.037 mol), and paraformaldehyde (1.13 g, 0.038 mol) were dissolved in toluene and heated under reflux for 72 h in a round-bottom flask. Schiff base product between aniline and vanillin was considered as impurities and minimized by using a low dielectric constant solvent, toluene. Product was purified by washing with approximately 500 mL of 1 N sodium hydroxide solution. After the wash, the toluene solution was dried with anhydrous sodium sulfate and filtered. Solvent was allowed to evaporate to leave yellow needle-like V-a crystals for collection. Yield was 83% as determined by weight.

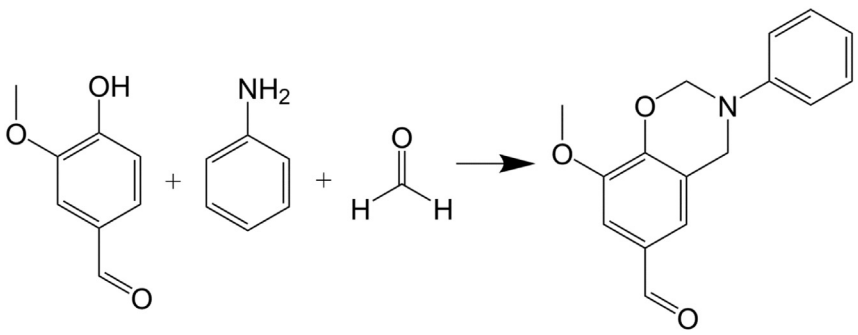
A sample of synthesized V-a was polymerized by heating at 220 °C for 2 h. This temperature was selected based on the DSC results, which indicated an exotherm at 246 °C.

FT-IR: 1692 cm^{-1} (C═O), 1600 cm^{-1} (C═C), 1495 cm^{-1} (Ar), 1144 cm^{-1} (Ar-O), 1234 cm^{-1} (O–CH_2), 1076 cm^{-1} (O–CH_3), 912 cm^{-1} (C–C, out of plane ring bending with an attached oxazine ring).

NMR: 3.93 ppm (3H, O–CH_3), 4.72 ppm (2H, Ar–CH_2-N), 5.54 ppm (2H, O–CH_2–N), 6.80–7.50 ppm (7H, Ar–H), 9.81 ppm (1H, HC═O).

2.2.2. Synthesis of (E)-61,64-dimethyl-N-((8-phenoxy-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methylene)-2,5,8,11,14,17,20,23,26,29,32,35,38,41,44,47,50,53,56,59,62,65-docosaoxaoctahexacontan-67-amine

(E)-61,64-dimethyl-N-((8-phenoxy-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methylene)-2,5,8,11,14,17,20,23,26,29,32,35,38,41,44,47,50,53,56,59,62,65-docosaoxaoctahexacontan-67-amine (hereinafter abbreviated as V-a-Jeff) synthesized from V-a and Jeffamine M1000 is shown in Scheme 3. V-a (0.211 g, 0.787 mmol) and Jeffamine (0.847 g, 0.847 mmol) were mixed and heated at 100 °C for 24 h in a round-bottom flask. A yellow liquid was obtained and used without further purification. Yield was 75%, as later determined by FT-IR and NMR.



Scheme 1. Synthesis of vanillin-aniline benzoxazine monomer from vanillin, aniline, and paraformaldehyde.