



Preparation and characterization of lignin based macromonomer and its copolymers with butyl methacrylate



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ABSTRACT

Copolymerization of butyl methacrylate (BMA) with biobutanol lignin (BBL) was achieved by free-radical polymerization (FRP) using a lignin-based macromonomer. The lignin-based macromonomer containing acrylic groups was prepared by reacting acryloyl chloride with biobutanol lignin using triethylamine (TEA) as absorb acid agent. From the results of elemental analysis and GPC, the average degree of polymerization (DP) of BBL was estimated to be five. A detailed molecular characterization has been performed, including techniques such as ¹H NMR, ¹³C NMR and UV–vis spectroscopies, which provided quantitative information about the composition of the copolymers. The changes in the solubility of lignin-g-poly(BMA) copolymers in ethyl ether were dependent on the length of poly(BMA) side chain. TGA analysis indicated that the lignin-containing poly(BMA) graft copolymers exhibited high thermal stability. The bulky aromatic group of lignin increased the glass-transition temperature of poly(BMA). In order to confirm the main structure of copolymer, (AC-g-BBL)-co-BMA copolymer was also synthesized by atom transfer radical polymerization (ATRP), and the results revealed that the copolymer prepared by ATRP had the same solution behavior as that prepared by FRP, and the lignin-based macromonomer showed no homopolymerizability due to the steric hindrance. In addition, the lignin-co-BMA copolymer had a surprisingly higher molecular weight than poly(BMA) under the same reaction condition, suggesting that a branched lignin based polymer could be formed.

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1. Introduction

Nowadays, it is urgent to explore a new renewable resources for the preparation of polymeric materials due to the rapid energy exhaustion and environmental awareness [1]. One of the feasible ways to mitigate and solve these problems is to use naturally renewable resources as raw materials [2] and produce green polymers [3]. However, the high cost in collection and purification of renewable materials has impaired the commercial applications of renewable polymers when compared to those of traditional petroleum-derived materials. As a result, the interest in the development of novel low-cost monomers as viable replacements for petroleum based resources to synthesize useful sustainable materials has received considerable attention [4–7].

Lignin, as a new class of abundant, inexpensive, intriguing aromatic and naturally renewable raw material, has been employed as a feedstock for the preparation of polymeric materials [8,9], and acted as a functional constituent which could improve the mechanical properties and thermal stability of existing petroleum based polymer in recent decades. Biomass-butanol lignin (BBL), an important byproduct of biomass-derived butanol obtained by using agricultural wastes (e.g. cornstalks and wheat straw) as raw material, has a similar chemical composition to that of traditional lignin. BBL was primarily treated as a waste and used as boiler fuel to produce steam and power due to its complex irregular macromolecular structure. The development of value-added BBL-based materials was regarded as an efficient method to decrease the cost of production of biomass-derived butanol and enhance commercial competitiveness. Currently, BBL has been employed as low-molecular weight phenols or aromatics to produce polymeric materials due to its low molecular weight and high chemical activity [10]. BBL has been reported to be used to prepare PF adhesives [11,12], biosorbents [13], activated carbon fiber [14], polyurethane foam [15], dispersant [16] and UV-absorbent coatings [17,18],

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which could offset some cost of the manufacturing of biomass-derived butanol and achieve more commercial affordability.

Generally, lignin was utilized as a macromonomer for polymer applications by blending with the traditional petroleum-based polymers without [19,20] or with surface chemical modification [21]. However, this approach had a disadvantage that the improvement of the compatibility between lignin and blended polymers was often limited. Recently, attention has been focused on “graft-from” strategies for functionalized lignins. Panesar et al. [22] reported that vinyl acetate (VA) could be successfully grafted on lignin through copolymerization using potassium persulfate as an initiator, which achieved to graft poly(VA) chains onto the lignin macromolecular structure. Compared with the former blending approach, this strategy could remarkably enhance the structure compatibility between lignin and grafted polymers [23].

Free radical polymerization is a robust technology, which has been employed to produce polymer for many decades. So the idea for the utilization of lignin by free radical polymerization was naturally conceived and implemented. However, the lignin contains phenolic hydroxyl groups that was proved to scavenge the free radicals [24] and lead to low monomer conversion and molecular weight [25]. Additionally, free radical polymerization of lignin containing vinyl groups was also displayed low efficiency due to the steric hindrance [26]. A great deal of efforts have been dedicated to substitute the phenolic groups in lignin by esterification to allow the polymerization to proceed. The prepare and polymerization of lignin derivatives with acetic anhydride were firstly reported by Dacunha et al. [27]. Lignin based macromonomers were obtained by reacting acetic anhydride with a kraft lignin and then copolymerized with methyl methacrylate (MMA) by free-radical polymerization. The copolymerization with MMA gave a “Linear” graft copolymer containing up to a lignin content of 40 wt.%.

Herein, BBL was designed to be a macromonomer with the capability to undergo free radical polymerization by the introduction of acrylic groups via the esterification with acryloyl chloride [28]. The biobutanol lignin based macromonomer (AC-g-BBL) was characterized by FT-IR and ^1H NMR. The copolymerization of AC-g-BBL and butyl methacrylate (BMA) was carried out via free-radical polymerization. The detailed molecular characterization, molecular weight, thermal properties and pencil hardness of (AC-g-BBL)-co-(BMA) copolymers were investigated. In comparison, the BBL-g-poly(BMA) copolymer was also synthesized by atom transfer radical polymerization (ATRP) [29,30].

2. Methods

2.1. Materials

Biomass-butanol Lignin (BBL) was obtained from Songyuan bairui bio-polyos Co. Ltd., China. Acryloyl chloride, 2-bromoisobutyryl bromide and Cu(I)Br were purchased from ARCOS and used as received. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was purchased from Aldrich and used as received. Azobisisobutyronitrile (AIBN, 99%) was recrystallized from hot methanol prior to use. Triethylamine (TEA), *N,N*-dimethylacetamide (DMAC), 1,4-dioxane were purchased from Nanjing Chemical Reagent Co., Ltd., and dried by using 4A molecular sieves for four days prior to use. Chemical agents like sodium hydroxide (NaOH), hydrochloric acid (HCl), *n*-hexane and so on were analytical grade and used as received.

2.2. Characterization

2.2.1. FT-IR analysis

Each sample was casted film and placed on a ZnSn window from THF solution (1% w/w) using attenuated total reflection Fourier

transform infrared (ATR-FTIR) method on a Nicolet(USA)IS10 instrument.

2.2.2. ^1H and ^{13}C NMR analysis

^1H and ^{13}C NMR spectra were measured using a Bruker Avance 500 MHz spectrometer. For ^1H NMR, 10 mg of samples were dissolved in 0.7 mL of CDCl_3 . For ^{13}C NMR, 20 mg of samples were dissolved in 0.7 mL of CDCl_3 . All chemical shifts were referenced to tetramethyl silane.

2.2.3. Thermal analysis

Thermogravimetric analysis (TGA) was performed on a TGA Q500 apparatus (TA instruments) under nitrogen at a rate of $10^\circ\text{C min}^{-1}$ from 30 to 800°C . Differential scanning calorimetry (DSC) measurements were run to measure the glass transition temperature (T_g) using a heating rate of $10^\circ\text{C min}^{-1}$, and data were collected from the second heating scan.

2.2.4. Elemental analysis

The carbon, hydrogen, oxygen (by difference), nitrogen and sulfur weight percentages of vacuum dried BBL were determined with a Vario Micro Elemental Analyzer (Germany).

2.2.5. UV analysis

UV-visible spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer in THF and at room temperature. The average extinction coefficient of each copolymer was calculated from UV-visible measurements of three different copolymer concentrations (0.029, 0.058, and 0.087 g L^{-1}).

2.2.6. GPC analysis

The average molecular mass and molecular mass distribution of the samples were determined by gel permeation chromatography (GPC) (Waters1550) with tetrahydrofuran (THF) as the eluting solvent. All samples were dissolved in THF at a concentration of 1 mg mL^{-1} and filtered ($0.45\ \mu\text{m}$, PTFE syringe filter) prior to analysis. The columns were calibrated with polystyrene standards.

2.2.7. Water contact angle measurement

The apparent contact angle were performed by placing a $10\ \mu\text{L}$ water droplets on the surface of the films and then imaged after 20 s [15]. The result of each sample was an average of 10 measurements.

2.2.8. Pencil hardness test

Pencil hardness of the film was determined on the pencil hardness measurement apparatus (Sheen720N) by using walter pencils (9B–B, HB, F, H, and 2H–9H) with fixed angle 45° by loading 765 g.

2.3. Purification of biobutanol lignin

About 100.0 g BBL was dissolved in 1000 mL distilled water with pH to 12.5, which was adjusted by a 20 wt.% aqueous solution of NaOH. BBL was then precipitated by the switch of based solution into an acidic solution with a pH of 2.0–3.0 by using a 10 wt.% HCl aqueous solution. The precipitated BBL was filtered and repeatedly washed with dilute HCl (pH = 2.0) to exchange sodium counter ions [29], and then washed with distilled water until the washing water turned neutral. After the precipitation was dried under vacuum until a constant weight at 40°C , the purified BBL was obtained.

2.4. Acetylation of biobutanol lignin

The purpose of acetylation of BBL is to determine the aliphatic and phenolic hydroxyl contents. The procedure could be described as: 200 mg BBL was dissolved in a mixture of pyridine (10 mL) and acetic anhydride (10 mL), and stirred at room temperature for 72 h

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