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Facile synthesis and characterization of urushiol analogues from tung oil via ultraviolet photocatalysis

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ABSTRACT

In this work, the urushiol analogues (CAT-ME) carrying the functional groups of double bonds and phenolic hydroxyls were synthesized by Friedel-Crafts alkylation reaction of methyl eleostearate (the main component of tung oil) with catechol via ultraviolet photocatalysis. By comparison of catalytic results of different photoinitiators, it was found that cationic photoinitiators (triarylsulfonium salts) could be used to catalyze this alkylation reaction, which could not only dramatically boost the yield (71%) of the urushiol analogues, but also greatly shorten the reaction time (8 min) at a low UV light (100 W). And the chemical structures of the target compounds were also confirmed by Fourier transform infrared spectroscopy (FTIR), ultraviolet and visible spectroscopy (UV–vis), nuclear magnetic resonance spectroscopy (NMR) and liquid chromatography-mass spectroscopy (LC–MS). In addition, the photoactivity of the urushiol analogues was also discussed and the results showed that the UV-cured polyurethane films mixed with CAT-ME had excellent mechanical property and thermal stability, and the gel fraction of the film mixed with 15% CAT-ME reached 99.5%, and the tensile strength was up to 25.07 MPa while the breaking elongation increased by 4.57%. Thus, this approach of photocatalysis using cationic photoinitiators as catalysts showcases a promising method to direct other chemical reactions and provides a platform to guide the further modification of other unsaturated natural oil, expanding the application of vegetable oil.

1. Introduction

In recent decades, excessive consumption of fossil resources has led to environmental pollution problems and limits the development of natural organic polymers, seriously affecting the daily lives of people. To meet the long-term demand of sustainable development and the requirement of atom economy, many governments and researchers are devoted to looking for renewable energy source to alternate the traditional petroleum-based fuels [1–3]. Biomass, a green and clean feedstock derived from plant or aquatic sources, can be transformed into a large variety of liquid chemicals [4,5] and polymeric compounds [6,7] such as biodiesel [8] and polyurethane [9–11], by thermo-chemical [12,13] or biological conversion, and has increasingly received much attention in a wide variety of applications, such as in the fabrication of varnishes, paints or other related materials.

Vegetable oils (such as soybean oil, castor oil and tung oil) with 1–3 unsaturated double bonds can be used for the production of biocomposite [14] and bio-based polyurethanes materials [15,16]. Thus, they have recently got much attention to be used as the renewable and sustainable source for producing chemical productions. Among these natural vegetable oils, tung oil is comprised of a conjugated triene on the triglyceride molecule and classified as a conjugated drying oil. In addition, tung oil possesses the advantages of fast drying, high water resistance and hardness due to its high level of unsaturation [17], which endow tung oil numerous applications in the preparation of coating materials [18,19], varnishes [20,21], reactive diluents [22] and polyurethanes [23,24]. In recent years, the modification of tung oil with functional molecules has been attained increasing attention. One of the conventional methods for the modification of tung oil is basing on thermal polymerization [25], but the resulting products are viscous oils or weak rubbery films, which possess little utility for structural materials. In addition, tung oil is also generally modified via Diels-Alder reaction [26] based on its conjugated double bonds. However, for the modification of tung oil via Diels-Alder reaction, the long aliphatic chains of tung oil still results in the weak intermolecular interaction to restrict the practical applications. Therefore, the application market for

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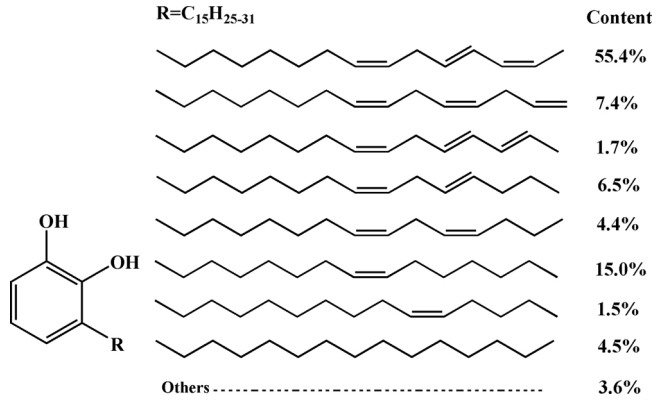


Scheme 1. Structure of typical urushiol in Chinese lacquer.

tung oil and its derived commodity chemicals is still at the infancy stage, and should be greatly gaining momentum.

Urushiol, the major constituent of raw lacquer, is a catechol derivatives mainly composed of the meta substitute of a C15 unsaturated hydrocarbon chain with one to three double bonds [27]. And the structure of typical urushiol is shown in Scheme 1. The polyurushiol [28] is widely used in the fields of coatings, finishes, and adhesives, because of its excellent physico-chemical property including anticorrosion, solvent resistance, thermal stability, and super insulativity. However, the production of urushiol is limited. Therefore, the synthesis of urushiol analogue has attracted the interest of researcher. The Friedel-Crafts alkylation reaction of tung oil with catechol is expected to be an excellent alternative to develop novel urushiol analogues. Traditionally, this alkylation reaction of aromatic compounds is carried out using $AlCl_3$, HF, or sulfuric acid as catalyst. However, these used catalysts can result in environmental problems, and require considerably complex procedures to conduct post-processing to purify products. Our previous work has synthesized urushiol-like compounds from tung oil using silica-supported phosphotungstic heteropoly acid catalyst [29]. But the conventional heating reactions not only require high temperature, but also long time, with low yield and efficiency.

Photocatalysis, a green and well-accepted optical technology with the energy source of sun-light [30,31] or UV-light [32,33], has greatly developed in recent years, due to its extensive applications in various fields across a wide range of research and commerce areas. Photoinitiators, an important component of UV curing system, especially cationic photoinitiators, such as diaryliodonium and triarylsulfonium salts [34,35] with non-nucleophilic anions such as BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, not only can be widely used in the photopolymerization whether under UV-light [36] or visible-light [37], but also can trigger some chemical reactions, such as click reaction [38–40]. Chen et al. have synthesized norbornyl epoxidized linseed oil and investigated the effect of divinyl ether concentration and types of divinyl ether on the photopolymerization reaction [41]. Dillman have prepared acrylated castor oil under solventless conditions, which possessed highly efficient photopolymerization processes [42]. Feng et al. have developed a solvent-free method to prepare soybean oil-based polyols by thiol-ene click reaction under UV-irradiation and then obtained biobased polyurethanes [43]. Desroches et al. have reported the radical addition of 2-mercaptoethanol onto oleic acid under UV light with mild conditions of room temperature and without any photoinitiator [44]. Recently, our research has found that the Friedel-Crafts alkylation of tung oil with catechol can be carried out to prepare urushiol analogues in the presence of cationic photoinitiators under UV light.

The aim of the present study was to synthesize novel urushiol analogues from tung oil via ultraviolet photocatalysis, and explore the photoactivity and application of the obtained urushiol analogues. To be specific, eleostearic acid glyceride, the main component of tung oil, was firstly transformed to methyl eleostearate (ME) via transesterification. Then the urushiol analogues (CAT-ME) were synthesized by Friedel-Crafts alkylation of methyl eleostearate (ME) with catechol (CAT) using photoinitiators as catalysts under UV light. Then, the photoactivity of the novel urushiol analogues was also discussed.

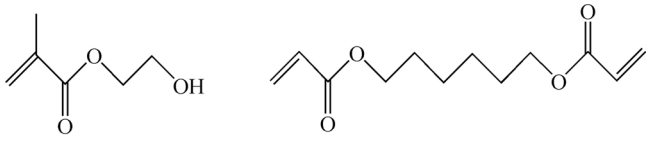
2. Experimental

2.1. Materials

Tung oil containing 74.269% eleostearic acid, 6.578% oleic acid, 5.294% linoleic acid and 4.043% saturated fatty acid (ESI, Fig. S1, S2) was purchased from Shandong Jiuxing Chemical Co., Ltd., China. The density, viscosity and iodine value of tung oil were 0.935 ± 0.01 g/mL, 3.0 ± 0.1 Pa·s and 168 g/100 g, respectively. Methanol, sodium hydroxide, catechol, sulfuric acid, phosphoric acid and acetic acid were provided by Tianjin Fuyu Fine Chemical Co., Ltd., China. Petroleum ether, ethyl acetate and acetone were obtained from Tianjin Damao Chemical Reagent Factory. Polyurethane acrylate (PUA-2665) was purchased from Power Dream Chemical Co., Ltd., China. The molecular weight and viscosity of PUA-2665 were 3000 g/mol and 1000 mPa·s, respectively. The reactive diluting acrylates of 2-hydroxyethyl methacrylate (HEMA) and 1, 6-hexanediol diacrylate (HDDA) were purchased from Sartome Guangzhou Chemical Co., Ltd., China. The cationic photoinitiators including bis(4-methylphenyl)iodonium hexafluorophosphate (DAI) and (4-phenylthio)phenyl diphenyl sulfonium hexafluorophosphate (TAS), and free radical photoinitiators including 2-hydroxy-2-methylpropiophenone (PI-1173), 1-hydroxycyclohexyl phenyl ketone (PI-184), 2,4,6-trimethyl benzoyl diphenylphosphine oxide (PI-TPO) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (PI-819) were purchased from Eternal Materials Co., Ltd., China. The specific structures of the used reactive diluents, photoinitiators and resin were shown as Scheme 1–5. And the characterization of cationic photoinitiators (TAS and DAI) and PUA-2665 were shown in Fig. S3 and Fig. S4 in supporting information. Tung oil, polyurethane acrylate, reactive diluting acrylates and photoinitiators used in this study were industrial products, the degree of purity of which was up to 95%, and the other chemicals were analytical reagent (AR). The water used in each experiment was distilled water.

2.2. Preparation of methyl eleostearate (ME)

Tung oil (87.2 g) was added to a three-necked round bottom flask (250 mL) equipped with a reflux condenser and a stirring paddle (220 r/min), and then was heated to 70 °C using a thermostat water bath. Therewith, sodium hydroxide methanol solution (the molar ratio of methanol to tung oil is 6:1, the weight of NaOH was 1 wt% of the weight of tung oil) was added into the round bottom flask, and the reaction mixture was mechanically stirred for 1 h. Thereafter, the pH value of the reaction mixture was neutralized to 6.5 ~ 7.0 via adding phosphoric acid. Then, the reaction mixture was instantly transferred to a pear-shaped funnel (250 mL), and stood for a while to form two layers. The upper layer was collected and washed 3–4 times with hot distilled water to obtain the targeted product (methyl eleostearate). Furthermore, methyl eleostearate was purified by distilling off the unreacted methanol using a rotary evaporator, and dried by anhydrous sodium sulphate. Finally, the $AgNO_3$-silica gel column chromatography was used to further purify methyl eleostearate. The detailed preparation



Scheme 2. The structural formulas of reactive diluents.