



# Triazolinedione-based Alder-ene modification of eucommia ulmoides gum to flexible polyelectrolyte and ion gel

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## ABSTRACT

Eucommia ulmoides gum (EUG) is a biomass-based polymer, and has a number of double bonds on the backbone, which can be post-functionalized. 1,2,4-Triazolone-3,5-dione derivative was synthesized and used to modify EUG by Alder-ene reaction, yielding a viscous modified EUG polyelectrolyte bearing 1,2,3-triazolium and polyethylene glycol pendants, which exhibited a relatively high ionic conductivity of  $1.3 \times 10^{-5} \text{ S cm}^{-1}$  at 30 °C. The viscous EUG polyelectrolyte was further crosslinked by bis(1,2,4-triazolone-3,5-dione), and transformed to a solid state with a tensile strength of 2.0 MPa and an elongation at break of 150%. The crosslinked flexible EUG polyelectrolyte can take up ionic liquids with good compatibility to form the ion gel, and demonstrated an enhanced ionic conductivity of  $1.4 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C when containing 50 wt% of ionic liquid, while maintaining good mechanical properties, which will have a potential application in the field of dielectric elastomer and flexible electronic devices.

## 1. Introduction

Gel polymer electrolytes (GPEs) are attracting increasing interest for electrochemical technologies and have widely applications in the field of batteries [1–3], organic thin-film transistors [4], and solar cells [5]. Especially in the batteries engineering, GPEs are considered to be one of the ideal materials to instead of traditional liquid electrolytes, because the latter one has the drawbacks such as poor safety, limited voltage, low energy density, and poor cycling performance [6–8]. Besides, GPEs with proper bending and tensile strain (flexibility and stretchability) could not only endow batteries with wearable and miniaturization, but also more durable [9]. Therefore, designing multifunction GPEs with tremendous performance in electronic devices is a recalcitrant challenge.

GPEs are polymers swollen with a substantial amount of liquid electrolytes containing proper high-boiling solvents and electrolyte salts [10,11]. Ion transport of GPEs depends on cations and anions diffusion in electrolyte solvents, as a result, the ionic conductivity ( $\sigma$ ) of GPEs is close to liquid electrolytes. Polar and non-volatile are two fundamental characters of the electrolyte solvents, like propylene carbonate, diethyl carbonate, dimethyl carbonate, *g*-butyrolactone, and

DMF, etc. However, undesired reactions between the electrode and the liquid organic electrolyte lead to the potential risk for the batteries [12]. Instead of organic solvents by inert electrolytes may help to solve this problem. Ionic liquids (ILs), also known as room-temperature molten salts, perform excellent physical and chemical properties. They are famous for their non-flamer and chemical inactivity, and are widely recognized as “green solvents” [13–16]. To raise the lithium battery with the level of safety and energy density, one of the effective strategies was replacement of the conventional, flammable and volatile, organic solutions electrolyte with IL-based electrolytes [17]. Polymers incorporating with ILs to obtain the so called “ion gel”, a new kind of GPEs, offered the improved thermal stability, security, and mechanical properties, which has received an upsurge of interest recently [18,19]. Watanabe reported the synthesis of highly ion-conducting rubbery gel electrolytes via in situ polymerization of vinyl monomers in imidazolium IL. This ion gel exhibited dramatic  $\sigma$  closed to  $10^{-2} \text{ S cm}^{-1}$  at ambient temperature [20]. Generally, ion gel has the disadvantage of lack of strength. Lodge reported a ABA triblock polymer (10 wt%) in IL to provide a kind of ion gel, and this gel can be chemically cross-linked in a second annealing step to improve the mechanical strength of materials. The  $\sigma$  of this “ion gel” was above  $10^{-2} \text{ S cm}^{-1}$  at 100 °C, which

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was as high as 2/3 of that of the pure IL. The tensile strength of this material increased from  $0.8 \times 10^5$  Pa to  $4.0 \times 10^5$  Pa after crosslinking [21].

With the strengthened awareness of fossil crisis and environmental pollution issues, people tried to replace the fossil-based resource by the renewable resource. Cui reported a cellulose-based composite non-woven as lithium-ion battery separator instead of polyolefin microporous separator. Cellulose is a biomass resource with excellent thermal stability, and the cellulose-based separator performed the superior thermal resistance compared with the traditional polypropylene separator [22]. *Eucommia ulmoides* gum (EUG), extracted from the sustainable resource of *Eucommia ulmoides* oliver, a large xylophyta and mainly grown in China, is a natural biomaterial possessing the duality of rubber and plasticity with a molecular structure of *trans*-1,4-polyisoprene and crystallinity. However, the application of modified EUG was rarely reported. Modifying EUG in chemistry is an efficient way to obtain functional polymer material. Epoxidation, halogenation, and hydrogenation are conventional chemical modification methods to EUG. However, these methods are harmful to environment. Near the past several decades, a special click reaction of triazolinedione (TAD)-based Alder-ene chemistry with unsaturated hydrocarbon substrates has gained rapidly growing attention, because this reaction is metal-free, quantitative, low energy consumption, and high yield, which greatly met the demand of green chemistry. TAD is generally considered as the most reactive dienophiles and enophiles [23–27], and the Alder-ene reaction is a versatile way to functionalize the non-conjugation-alkene substrates. Saville introduced TAD-based modification to nature rubber as early as 1970s [28]. Meanwhile, TAD-based modification can be processed in the alkene crosslinking reaction. Prez reported bifunctional TAD for the chemical crosslinking of crude plant oils, the gelation occurred within minutes and whole progress can be monitored visually, and the glass transition temperature ( $T_g$ ) of the crosslinked plant oils increased to 70 °C [29]. These illustrated that TAD-based modification has a great potential in polymer science. Herein, the natural unsaturated polyolefin EUG with rich resources was modified by substituted TADs, 4-(2-(4-(polyethylene glycol)-1,2,3-triazol)ethyl)-(1,2,4-triazoline-3,5-dione) (PTT) and 4,4'-(4,4'-)hexylbis(1,2,4-triazoline-3,5-dione) (bTAD), and the crosslinked EUG was used as a substrate to load IL to obtain the ion gel. Initially, EUG was reacted with PTT at room temperature to increase the compatibility of EUG and ILs, because pure EUG was nonpolar and caused phase separation when mixed with IL, and then bTAD was reacted with modified EUG to form network structure, making the mechanical properties and thermal resistance be improved. The obtained EUG-based ion gel preformed an enhanced ionic conductivity and good mechanical properties, which will have a potential application in the field of dielectric elastomer and flexible electronic devices.

## 2. Experimental

### 2.1. Materials

*Eucommia ulmoides* gum (EUG) was purchased from Xiangxi Laodie Biology Company. Bis(trifluoromethane)-sulfonimide lithium (LiTFSI), iodomethane (CH<sub>3</sub>I), and methoxypolyethylene glycol 350 (PEG350) were purchased from Shanghai Dibo Chemical Reagents Company. Ethyl carbazate, sodium azide (NaN<sub>3</sub>), sodium hydride (NaH), 2-chloroethyl isocyanate, and 1,4-diazabicyclo[2.2.2]octane were purchased from Shanghai Energy Chemical. *L*-Ascorbic acid (99%), tetrahydrofuran (THF), dichloromethane (DCM), chloroform (CHCl<sub>3</sub>), acetonitrile (CH<sub>3</sub>CN), and CuSO<sub>4</sub>·5H<sub>2</sub>O were purchased from Shanghai Chemical Reagents Company. Solvents were distilled over drying agents prior to use. 1,4-Dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides (DABCO-Br) and bTAD were synthesized according to the literature [23]. Propinyl-methoxypolyethylene glycol was synthesized according to the literature [30].

### 2.2. Characterization

<sup>1</sup>H (500 MHz), <sup>13</sup>C (125 MHz), and <sup>19</sup>F (471 MHz) NMR spectra were recorded on a Bruker DRX500 spectrometer with tetramethylsilane as an internal standard in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> at room temperature. FT-IR spectra were recorded on a Nicolet Nexus 670 in the region of 4000–400 cm<sup>-1</sup> using KBr pellets for transmission or in CHCl<sub>3</sub> solution at 20 mg mL<sup>-1</sup> for attenuated total reflectance (ATR) measurements. Gel permeation chromatography (GPC) was used to calculate the relative molecular weight and polydispersity equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm with particle size of 5 mm; pore diameter of 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å). The injection loop, the columns and the RI detector were thermostated at 35 °C in the same oven. The eluent was a solution of LiTFSI (0.05 M) and 1-(*n*-butyl) imidazole (0.05 M) in THF. The samples were dissolved in eluent solution at 0.2 wt % before being filtered on a polytetrafluoroethylene (PTFE) filter with 0.22 μm diameter pore size. Number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) of polymer were calculated according to a calibration curve established with polystyrene standard. Thermal gravimetric analysis (TGA) was performed by an SDT851e/SF/1100 °C TGA instrument under nitrogen flow at a heating rate of 30 °C min<sup>-1</sup> from 25 to 800 °C. Differential scanning calorimetry (DSC) was performed on a Q2000 DSC instrument with a liquid nitrogen cooling system and a nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. The samples were first heated from 40 to 100 °C at a rate of 20 °C min<sup>-1</sup>, equilibrated 3 min to eliminate the thermal history; then cooled to -90 °C at a rate of 10 °C min<sup>-1</sup>, equilibrated 3 min again; finally, heated to 100 °C at a rate of 10 °C min<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was used to measure the ionic conductivity of polymers at 30 °C, performed using a CHI 660E electrochemical workstation (Shanghai Chenhua Equipments, China). Samples were placed between two copper plates inside a spacer cut from PTFE tape with a small hole in the center, which constructed a sandwich system. Frequency sweeps were performed isothermally from  $1.0 \times 10^5$  Hz to 0.01 Hz by applying a sinusoidal voltage of 50 mV. The  $\sigma$  of polymers was calculated according to the following equation:  $\sigma = D/(SR)$ , where 'D' is the thickness of the polymer layer, 'S' is the area of polymer layer, and 'R' is the bulk resistance extracted from a Nyquist plot of impedance spectroscopy, which is approximately equal to the numerical value of the diameter of the semicircle or the intercept of the straight line on the Z' axis at high frequencies. The measurements were conducted under a closed atmosphere with P<sub>2</sub>O<sub>5</sub> in it to exclude the presence of humidity in the measurement chamber. The mechanical property was measured using a universal testing machine (HY-0580, Shanghai Hengyi Test Instrument Co., Ltd.) at a stretching speed of 20 mm/min with the sample straps of about 0.8 cm wide and 1.5 cm long. The hydrodynamic diameter was determined by means of dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He–Ne laser (633 nm, 4 mW). The Nano ZS instrument incorporates noninvasive backscattering (NIBS) optics with a detection angle of 173°. Atomic force microscopy (AFM) observation was performed on an SPM AJ-III atomic force microscope at a measurement rate of 1.0005 Hz in the tapping mode, and AFM image was obtained at room temperature in air. Samples were prepared by drop coating a THF solution at 0.05 mg mL<sup>-1</sup> on a freshly cleaved mica surface, and were then air-dried at room temperature.

### 2.3. A general modification process of EUG with 4-(2-(4-(polyethylene glycol)-1,2,3-triazol)ethyl)-(1,2,4-triazoline-3,5-dione)

EUG (0.10 g, 1.5 mmol) was dissolved in 5 mL CHCl<sub>3</sub>, and the required amount of PTT (0.66 g, 1.1 mmol) in 5 mL CHCl<sub>3</sub> was added into the above solution rapidly at room temperature while stirring vigorously. The PTT-modified EUG (PTEUG) (0.70 g, 1.4 mmol) was purified by precipitating in 100 mL of diethyl ether at least three times with

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