



Highly efficient preparation of hyperbranched epoxy resins by UV-initiated thiol-ene click reaction



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ABSTRACT

Hyperbranched epoxy resins (HEPs) attract an increasingly interest due to their remarkably reinforcing and toughening properties on thermoset. A major challenge for HEPs is the serious environmental pollution resulted from the large amount of organic solvents used during tedious synthetic procedure. Another challenge is low yield and low epoxy content of HEPs, resulting in low crosslinking density and impairing mechanical strength and compatibility with matrix. Here we report a fast and environmentally friendly approach to addressing these challenges using a UV-initiated thiol-ene click reaction. The new synthesis process has been used to prepare not only hyperbranched epoxides with high epoxy content, and also many kinds of glycidyl ether epoxy resins (mono-epoxide, di-epoxides, tri-epoxides) based on thiols precursors and allylglycidyl ether. Their chemical structures and molecular weights were characterized by FT-IR, ¹H NMR, electrospray ionization mass spectrometry (ESI-MS) and GPC spectra. All the click reactions took only 5–10 min of UV radiation at room temperature and show very high yields between 98.1 and 99.8%, and epoxy equivalent weight of all the epoxy resins is very close to its theoretical value. This fast and environmentally friendly process may open a new avenue for the design and synthesis of HEPs as well as common epoxy resins.

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1. Introduction

Hyperbranched epoxy resins (HEPs) are versatile thermosetting additives [1] and have been used in coatings, adhesives, electrical insulating materials, laminates and encapsulants, and multifunctional additive for reinforcing and toughening diglycidyl ether of bisphenol-A (DGEBA). Synthetic methods of HEPs mainly include (1) etherification between hydroxyl group and epichlorohydrin [2,3], (2) esterification between carboxyl group and epichlorohydrin [4,5], (3) oxidation of double bonds [6,7], (4) proton transfer polymerization [8–10] or atom transfer radical polymerization (ATRP) [11,12], and (5) hydrosilylation [13,14]. HEPs prepared by the above methods [2,4,9] but the last one [14] usually contained low epoxy content because of many hydroxyl groups, impairing thermal performance or tensile strength of DGEBA although increasing toughness, resulted from low crosslinking density and

poor compatibility with DGEBA. Many experiments [4,13,15] have confirmed that high epoxy content of HEPs could remarkably increase compatibility between HEPs and DGEBA and reinforce their tensile strength and heat-resistance. Therefore, an efficiently synthetic method about HEPs with high epoxy content is still a challenge.

Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin as well as HEPs, the most widely used epoxy resin in industry, is manufactured using time-consuming and complicated synthetic process. The open-ring and close-ring reactions involved in synthesis employ large quantities of organic solvents and water to wash and remove the byproduct NaCl. The water discharged from the process causes serious pollution. Considerable efforts [16] have been devoted to exploring new manufacturing methods and routes. The esterification [4,5] and etherification routes for preparing epoxy resins (EPs) also have similar environmental problems that large quantities of organic solvents are used and a lot of polluted water with byproduct NaCl are produced. Oxidation of double bonds [6,7], on the other hand, is a tedious process with low conversion efficiency besides the requirement of acid as catalyst, producing

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some acid waste water. The proton [8–10] or atom radical [11,12] transfer polymerization method involves the preparation of epoxy monomers, which is a tedious and complicated process because of water washing and organic solvent separation. Our group reported the use of hydrosilylation [13,14] to overcome the environmental pollution of water washing and organic solvent extraction. However, the multi-step reactions and expensive platinum catalyst used in the preparation of HERSS (hyperbranched epoxy resins with silicone skeleton) hinders its up-scaling and industrial application. We also have tried to prepare EPs [17,18] through a thiol-ene Michael addition between functional mercaptopropionate and glycidyl methacrylate, showing some extraordinary properties of click reaction [19–21], including close to theoretical yields, harmless byproducts and high selectivity. The thiol-ene click reaction may be performed under solventless conditions or in environmentally benign media (such as water), which simplifies product isolation and opens an avenue for synthesizing EPs. Another important advantage of the thiol-ene click reaction is that the resultant epoxy resins have excellent stability due to the absence of hydroxyl group, leading to a much simpler synthetic process than the traditional chromatographic column separation synthesis of hydroxyl-free EPs. Although at lower reaction temperature than other methods, the thiol-ene Michael addition between mercaptopropionate and glycidyl methacrylate not only spent long reaction time (about ten hours) [18] and but also need accurate condition to avoid self-polymerization of glycidyl methacrylate. A simple, rapid, energy-saving and environment-friendly method for synthesizing EPs still remains to be a major challenge.

In this paper, we present a fast and environmentally friendly process for preparing HEPs and other EPs monomers by integrating energy-saving UV-initiated technology and highly efficient thiol-ene click reaction [22]. A series of epoxy resins, including mono-epoxide, di-epoxides, tri-epoxides and hyperbranched epoxy resins, were synthesized through the thiol-ene click reaction between their precursors and allylglycidyl ether (AGE) via UV initiation. Compared with the above reported methods, all the click reactions were performed at room temperature and took only 5–10 min aided UV radiation, moreover, high yields of about 98.1–99.8% were achieved in all the click reactions.

2. Experimental

2.1. Main materials

Phenyl methanol, diethylene glycol (DEG), ethylene glycol (EG), 1,4-butanediol (BDO), 1,3,5-Tris(2-hydroxyethyl)isocyanurate (THEIC), tri(hydroxymethyl)propane (TMP), 3-mercaptopropionic acid (MPA), *p*-toluenesulfonic acid, allylglycidyl ether (AGE), and organic solvent were all of analytical grade and were sourced from Shanghai Chemical Reagent Co., Ltd. 1-Hydroxycyclohexyl phenyl ketone (photoinitiator 184) was sourced from BASF Chemical Company. Hydroxyl-ended hyperbranched polyesters (HyPer H102 and HyPer H103) were supplied by Wuhan Hyperbranched Polymer Resins Science & Technology Co. Ltd. They were used in this study without further purification unless noted.

2.2. Characterization

FT-IR measurements were performed on a Bruker Vector 33 spectrometer using sealed cell (KBr 0.5 mm). ¹H NMR measurements was conducted on an AVANCE III-400 (Bruker) nuclear magnetic resonance spectrometer using DMSO-*d*₆ or CDCl₃ as solvent. Molecular weight and polydispersity index (PDI) of hyperbranched polymers were measured by sol gel permeation chromatography (GPC) system (Agilent PL-GPC 50) using a PL-

RTLS 15/90 dual-angle LSD as a detector and THF as the eluent. The molecular weights of other small molecular epoxy resins were measured by electrospray ionization (ESI) quadruple time-of-flight mass spectrometer (Agilent 6520 Q-TOF LC/MS) with a standard ESI source in the positive-ion mode. The epoxy equivalent weight of all the epoxy resins was measured and calculated by the standard method (ASTM D-1652).

2.3. Synthesis of epoxy resins

2.3.1. Synthesis of hyperbranched polyester epoxy resins

Firstly, thiol-ended hyperbranched polyesters (THBP-12 and THBP-24) were prepared by an esterification between MPA and hydroxyl-ended hyperbranched polyesters (HyPer H102 and H103), respectively. And then hyperbranched polyester epoxy resins (EHBP-12 and EHBP-24) were synthesized by a UV-initiated thiol-ene click reaction between AGE and thiol-ended hyperbranched polyesters. The typical synthesis scheme of hyperbranched polyester epoxy resin (EHBP-12) is illustrated in Scheme 1 as an example.

HyPer H102 (11.79 g, 0.01 mol), MPA (19.11 g, 0.18 mol), toluene (50 mL), and *p*-toluenesulfonic acid (0.54 g) were added into a four-necked flask equipped with stirrer, cooler, nitrogen inlet and water-trap (Dean-Stark) to react for about 10 h at reflux temperature of about 353 K under mechanical stirring. The resulting solution was washed for 3 times using 5 mL NaOH solution (5 wt%). Na₂SO₄ was added to the organic layer and maintained overnight. After the solvent was removed under reduced pressure, a yellowish liquid of about 21.27 g (thiol-ended hyperbranched polyester polymer containing 12 mol thiol groups, THBP-12) with a yield of 95.1% was obtained by using a similar process as 1,3,5-Tris(2-hydroxyethyl)isocyanurate tris(3-mercaptopropionate) THMP [18]. THBP-12 (3.35 g, 0.0015 mol), AGE (2.05 g, 0.018 mol), photoinitiator 184 (0.10 g) and some organic solvent were added into a flask, which was exposed to a medium pressure mercury lamp with power density of 80W/cm² for about 10 min under magnetic stirring at room temperature. After organic solvent was removed under reduced pressure, a yellow liquid (hyperbranched polyester epoxy resins, EHBP-12) of 5.30 g with a yield of approximate 98.1% was obtained. The epoxy equivalent weight of EHBP-12 was about 309 g/mol, being close to its theoretical value of 301 g/mol.

Using a similar process of THBP-12, a yellowish liquid (thiol-ended hyperbranched polyester polymer containing 24 mol thiol groups, THBP-24) with a yield of 90.3% was synthesized based on hydroxyl-ended hyperbranched polyester polymer (HyPer H103) and MPA. And a yellow liquid (hyperbranched polyester epoxy resins, EHBP-24) of 10.90 g with a yield of approximate 98.6% was obtained based on THBP-24 (7.03 g, 0.0015 mol), AGE (4.11 g, 0.036 mol), photoinitiator 184 (0.22 g) and some organic solvent. The epoxy equivalent weight of EHBP-24 was about 314 g/mol, being close to its theoretical value of 311 g/mol.

2.3.2. Synthesis of mono-epoxide

The synthesis scheme of mono-epoxide is shown in Scheme 2. The synthesis of a typical example is described as follows. Phenyl methanol (3.24 g, 0.03 mol), MPA (4.77 g, 0.045 mol), toluene (30 mL) and *p*-toluenesulfonic acid (0.16 g) as a catalyst were added into a four-necked flask equipped with stirrer, cooler, nitrogen inlet and water-trap (Dean-Stark) to react for about 10 h at reflux temperature of about 353 K under mechanical stirring. The resulting solution was washed for 3 times using 5 mL NaOH solution (5 wt%). Na₂SO₄ was added to the organic layer and maintained overnight. After the solvent was removed under reduced pressure, a colorless liquid of 5.77 g was obtained, which proved to be phenyl methanol mercaptopropionate (PMMP) with a yield of 98.1%. FT-IR

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