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Thiol reactive polybenzoxazine precursors: A novel route to functional polymers by thiol-oxazine chemistry

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ABSTRACT

Thermally activated ring opening polymerization of benzoxazines plays an important role in the fabrication of high performance phenolic thermosets with enhanced thermal and mechanical properties. In the present work, a novel synthetic strategy based on 1,3-benzoxazine-thiol ring opening reaction for the functionalization of polymers is reported. For this purpose, thiol reactive main chain benzoxazine polymer (PBZ) was synthesized by the reaction of bisphenol-A, 1,6-diaminohexane and paraformaldehyde in toluene:methanol mixture (2:1, v:v) following the monomer synthesis procedure. The obtained polybenzoxazine precursor was then reacted at room temperature with various thiol compounds, namely thiophenol, 2-ethanethiol and 1-butanethiol in CH₃OH/CHCl₃ for 24 h. Successful incorporation of the thiol compounds to PBZ was confirmed by spectral and molecular weight characterizations. The thermally activated curing of the remaining benzoxazine rings occurs at lower temperatures than that reported for the conventional benzoxazines. The described strategy represents a unique approach not only for the polymer modifications but also for the preparation of high performance thermosets.

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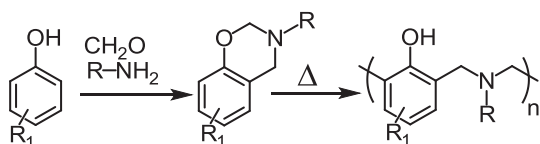
1. Introduction

Benzoxazine based thermosets has gained increasing interest in the polymer field as a superior alternative to Novolac and Resole type thermosetting. These materials provide many important features for high performance polymer applications. Low water absorption, high modulus, high strength, high glass transition temperatures, high char yield, chemical resistance, flame retardancy, long shelf life and more importantly they have very limited volumetric change and non-acid catalytic polymerization upon curing [1–4]. Another important feature of

polybenzoxazines is the simple synthesis of their monomers. Basically, any suitable primary amine and phenolic compound could form 1,3-benzoxazine monomers with formaldehyde (Scheme 1) [5–23]. The only possible drawback in monomer synthesis is the selection of functional groups on starting materials and solvent systems that suppress the reaction. However, many functional groups can be tolerated in synthesis conditions even aldehyde functional phenols can be used without decreasing the yield. Therefore, a vast molecular design is possible for polybenzoxazine thermosettings. The synthesis of polybenzoxazine is also simple, since it is thermally induced ring opening polymerization of 1,3-benzoxazine monomers which can be accomplished without any initiator or curing agent (Scheme 1) [24–32]. The polymerization temperature of benzoxazine monomers vary between 160 and 250 °C depending on the functional groups on the

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Scheme 1. Synthesis of a mono-functional benzoxazine monomer and its thermally activated polymerization.

monomers. Monomers containing labile hydrogens generally have low curing temperature that indicates the role of proton in polymerization mechanism [33–35].

For example, carboxylic acid and alcohol functional benzoxazines have low curing temperatures than benzene or alkyl functional benzoxazines and curing temperatures drop down to approximately 160 °C [35,36]. Hence, apart from thermally induced ring opening of 1,3-benzoxazines, alternative ring cleavage can be performed using Lewis or protic acids produced by photochemical means [37]. Thus, in some applications to decrease the polymerization temperature such additives are used. Apart from super-acids, thiols were recognized as having ability to cleave the oxazine ring by Gorodisher et al. This process was named as Catalytic Opening of the Lateral Benzoxazine Rings by Thiols (COLBERT reaction) which presumably proceeds by a nucleophilic addition and simultaneous ring-opening reaction [38]. In the first step, thiol acts as acid and protonates the amine of 1,3-oxazine ring and a cationic intermediate forms. Then, the resulting thiolate attacks to the bridging methylene carbon of N and O atoms and subsequent ring-opening of the 1,3-oxazine occurs (Scheme 2). This reaction has been found reversible by Endo et al. and the reversibility is mainly solvent dependent [39].

Even though its reversibility the reaction provides a significant advance in lowering the curing temperature of 1,3-benzoxazine monomers. In particular, COLBERT allows benzoxazine to polymerize even under ambient temperature. In our laboratory, we have utilized this reaction and demonstrated that cross-linked but additionally curable soft benzoxazine films can be prepared by simultaneous COLBERT and photoinduced thiol-ene reactions using difunctional thiol and diallyl functional benzoxazine [40]. Moreover, we have showed that benzoxazines can be used as a linker between two different polymers forming a block copolymer and COLBERT acted as a kind of thiol-oxazine click reaction to do so [41]. Another application of COLBERT was demonstrated by Endo et al. by using polyaddition reaction between a bisphenol A derived bifunctional benzoxazine and 1,6-hexanedithiol to afford the corresponding linear polymer [39].

By taking the advantage of abovementioned capabilities of COLBERT reaction in benzoxazine chemistry, it is clear that oxazine containing macromolecules can be modified by thiol functional molecules.

Although the earliest example dates back as early as more than a century ago, thiol based chemistries have recently been revitalized in polymer and materials science since they provide simple and versatile tool for various applications including polymer/network synthesis and efficient coupling chemistry in post-polymerization modifications [42–44].

There is a great interest to develop new thiol chemistries in order overcome drawbacks present in the existing approaches, further improving the chemistry and extending the fields of applications.

Hence, the present work attempts to use the relatively new thiol-oxazine chemistry for post functionalization of linear main chain polybenzoxazine precursors. As will be shown below, this objective is accomplished simply by mixing polybenzoxazine precursors with various thiols at ambient conditions.

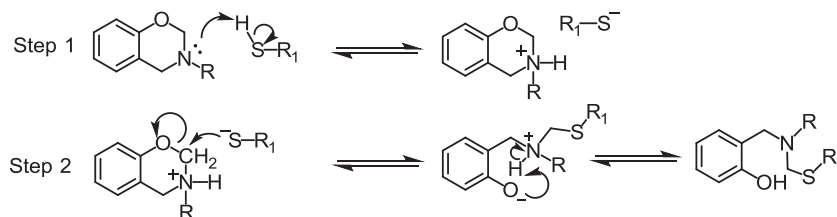
2. Experimental

2.1. Materials

Bisphenol A (Acros Organics, 97%), 1,6-diaminohexane (Acros Organics, 99.5%), paraformaldehyde (Aldrich, 99.5%), ethanol (Sigma–Aldrich, ≥99.8%), toluene (Merck, 99.9%), methanol (99%, Reiden-de Haen), chloroform (Alfa-Aesar, ≥99%), 1-butanethiol (Merck, ≥98%), thiophenol (Aldrich, 97%), thioethanol (Aldrich, ≥99.9%) were used as received.

2.2. Characterization

All ¹H NMR spectra were recorded on an Agilent NMR System VNMR5 500 spectrometer at room temperature in CDCl₃ with Si(CH₃)₄ as an internal standard. FT-IR analyzes were performed on a Perkin–Elmer FT-IR Spectrum One B spectrometer. Gel-permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Auto-sampler system consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX, USA), a combined light scattering (Model 270 Dual Detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Viscotek Corp.) The RI-detector was calibrated vs. polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers are expressed



Scheme 2. Plausible reaction mechanism for catalytic opening of the oxazine rings by thiols.

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