



High-performance recyclable cross-linked polyurethane with orthogonal dynamic bonds: The molecular design, microstructures, and macroscopic properties

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ABSTRACT

Polyurethane materials (PUs) have been widely used in industry and daily life due to the versatile chemistry. However, despite the rapid advance in synthetic chemistry, it still remains a significant challenge for the facile fabrication of PUs with a single cross-linked network embedded with excellent mechanical properties and recyclability. Herein, in this study, we proposed a simple strategy to fabricate a high-performance recyclable cross-linked PU and revealed the relationship between microscopic structure and macroscopic properties. The UPy (2-ureido-4-[1H]-pyrimidione) motifs were incorporated into the backbone chains of PUs, where the quadruple hydrogen bonding interactions between UPy dimers can significantly enhance the mechanical strength and toughness. Furthermore, a single small molecular Diels-Alder adduct was utilized as the chemical crosslinker, rendering the final cross-linked PUs healable and recyclable. The thermal reversibility of the Diels-Alder reaction was well verified by DSC and solid-state NMR spectroscopy. Notably, it was found that the incorporation of UPy motifs could enhance the strain-induced crystallization (SIC), leading to a large stress at break. The structural and dynamic changes induced by SIC were quantitatively addressed by proton multiple-quantum NMR spectroscopy and SAXS experiments, where SIC further imposed restrictions on the mobility of surrounding polymer chains in the soft domain and led to the change of microphase separated nanostructures. Overall, a simple strategy is proposed here for the facile fabrication of high performance recyclable PUs, and the detailed investigation here on the structure-property relationship may further provide insights into developing high performance polymeric materials.

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1. Introduction

Nature has evolved an intricate strategy to develop multi-scale hierarchical structures to impart the biomaterials with a

combination of superior chemical and physical properties; however, it remains a significant challenge to precisely design a healable and recyclable polymeric material with exceptional mechanical properties in a single network, despite the rapid advances in the synthetic chemistry [1–4]. One of the most straightforward approaches to enhance stiffness of polymers is to introduce cross-linkages in the polymer network. However, the introduction of permanent crosslinking usually leads to the sacrifice of extensibility during the tensile tests, and renders the materials unable to reprocess or recycle as well. In order to address these issues, dynamic covalent bonds have been widely

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incorporated into polymeric systems, where the dissociation and decrosslinking reaction can be triggered by external stimuli (such as heat, light, force, etc.) to enable self-healing and recycling [5–16]. Previously, we also incorporated thermoresponsive Diels-Alder (DA) adducts in the crosslinkages to yield recyclable and healable high performance materials [17–19]. Recently, the introduction of dynamic covalent exchange reactions, such as transesterification [9,20], olefin metathesis [21], transamination [22,23], etc., even enables the reprocessing and healing of thermoset polymers without damaging the integrity of polymer network. In addition, the sacrificial bonds, which was initially proposed to explain the molecular origin of the toughness of natural adhesives, fibers and composites [24] as well as bones [25], has been well developed in recent years and widely incorporated into the polymeric materials to improve the mechanical performance [26–29]. In fact, most of the dynamic physical bonds can play the role of sacrificial bonds, where they can break and reform during the tensile tests, acting as an effective avenue for stress energy dissipation and leading to fast recovery of mechanical properties. For example, Bao et al. utilized the dynamic Pt-imidazole coordination to prepare a super tough PDMS elastomer [30]. In fact, metal coordination, such as $\text{Fe}^{3+}/\text{Ca}^{2+}$ -carboxylic acid coordination [31–33], histidine-metal coordination [34], etc., has been well adapted in hydrogels to dramatically enhance the extensibility and fracture stress. Particularly, the well-known self-complementary quadruple hydrogen bonding interactions between UPy (2-ureido-4-[1H]-pyrimidione) dimers have been widely incorporated into polymeric materials for improving the mechanical properties [35–41], because the UPy dimers offer an appealing combination of high thermodynamic stability and rapid kinetic reversibility [42,43]. In order to increase the density of UPy motifs in the materials, UPy-containing molecules were often used as chain extenders [44–46], so that densely strong intermolecular hydrogen bonds can be formed, leading to an enhanced physical crosslinking density and thus the mechanical strength. Indeed, appropriate introduction of dynamic physical bonds has been well demonstrated as an effective and elegant approach for the fabrication of polymeric materials with enhanced mechanical performance [47–51].

Herein, we propose a simple strategy for facile fabrication of a recyclable and self-healing PU with superior mechanical strength and toughness by incorporating orthogonal dynamic covalent and physical interactions into a single network. Our design here aims to use HMA (5-(2-hydroxyethyl)-6-methyl-2-aminouracil) as the chain extender to incorporate UPy motifs into the backbone chains of PU, and then use the functional trihydroxy DA adduct to crosslink isocyanate-terminated PU under mild conditions. The key idea of our design is shown in Scheme 1. UPy motifs can form self-complementary quadruple hydrogen bonding interactions between each other, leading to denser H-bond assemblies including the H-bonds among isocyanate groups, which can overcome the intrinsic strength limitation of H-bonds and thus enhance the mechanical strength. Besides, the H-bonds can break and reform during the stretching deformation, resulting in efficient stress energy dissipation and thus an increase in toughness. Additionally, the strain-induced crystallization (SIC) is also enhanced by the incorporation of dense sacrificial hydrogen bonds, and thus leads to an increased stress at break. Here, it is worth mentioning that Zhang et al. [52] once simultaneously used UPy- and DA-based cross-linkers to obtain a dynamic dual-cross-linked poly (2-hydroxyethyl acrylate) (PHEA) with the capability of partial self-healing at room temperature and near complete healing upon heating. However, our design concepts and aims here are intrinsically different from theirs. First of all, we proposed an elegant approach to efficiently incorporate UPy and DA motifs in the PU materials to achieve comprehensive enhancement of mechanical

stiffness and toughness simultaneously, which are both tunable by changing the content of UPy or DA motifs. However, in the study of Zhang et al., [52] the improvement in mechanical properties was not mentioned or compared. Secondly, UPy motifs were incorporated into the backbone chains of PU in current study instead of into the crosslinkages in the study of Zhang et al. [52] As a result, the density of hydrogen bonding assembly in PU (i.e. content of UPy motifs) can be greatly increased as needed without being limited by the finite content of functional groups for chemical crosslinking in the study of Zhang et al. [52], leading to a broad range of tunable mechanical properties. Particularly, the elongation and stress at break can be over 2000% and 45 MPa, respectively. In brief, comprehensive enhancement of mechanical properties of PUs has been achieved in current study, and the thermal reversible crosslinker (DA adduct) can endow the PU healable and recyclable at an elevated temperature beyond 110 °C. The structure-property relationship of this material is also quantitatively addressed and characterized by a combination of various techniques, including proton multiple-quantum NMR spectroscopy, DSC, XRD, SAXS, DMA and so on.

2. Experimental section

2.1. Materials

Poly (ϵ -caprolactone) diol (PCL, $M_n = 2000$ g/mol), hexamethylene diisocyanate (HDI, 98%), guanidine carbonate, 2-acetylbutyrolactone, and Tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, 95%) were purchased from Sigma-Aldrich (USA). PCL was degassed for 2 h at 110 °C to remove moisture before use. Furfuryl alcohol (FA) was purchased from Acros Organics (Belgium, 97%), and was dried over anhydrous Na_2SO_4 and distilled under reduced pressure before use. 1,4-Butanediol (BDO) was bought from TCI (Shanghai, China), which was dried over CaH_2 prior to distillation under reduced pressure, and then further stored over 4 Å molecular sieves. All the other reagents were used as received without any further purification unless specified.

Synthesis of Diels-Alder adducts, FM. The crosslinker was prepared through a three-step process as described in the literature [18,53]. It is synthesized by a DA cycloaddition reaction between furfuryl alcohol and N-(2,3-dihydroxypropyl) maleimide. The synthesis pathway was shown in Scheme 2. The final product was dried in vacuum at 60 °C for two days. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 6.52 (br, 2H), 5.09 (s, 1H), 4.91 (br, 1H), 4.75 (br, 1H), 4.54 (br, 1H), 4.05 (d, 2H), 3.70 (m, 1H), 3.35 (d, 2H), 3.28 (d, 2H), 3.04 (d, 1H), 2.89 (d, 1H) ppm.

Synthesis of 5-(2-hydroxyethyl)-6-methyl-2-aminouracil (containing UPy motif): 5-(2-hydroxyethyl)-6-methyl-2-aminouracil (HMA) was synthesized according to the procedure reported in the literature [54], as also shown in Scheme 3. A mixture of 2-acetylbutyrolactone (2.2 mL, 20 mmol) and guanidine carbonate (1.5 g, 20 mmol) was refluxed with absolute ethanol (20 mL) in the presence of triethylamine (5.5 mL, 40 mmol) for 1 h. The mixture became clear, which was later precipitated to yield a pale yellow solid. The reaction was continued for 4 h, and then the precipitate was filtered and washed with ethanol, and finally dried in vacuum to afford 1.16 g product (69%) as a white solid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 2.02 (s, 3 H), 2.43 (t, 2 H), 3.30 (t, 2 H), 4.51 (s, 1 H), 6.63 (s, 2 H), 10.85 (s, 1 H) ppm.

Synthesis of PU materials. The procedure for the fabrication of PU material was shown in Scheme 4. Poly (ϵ -caprolactone) diol (PCL, $M_w = 2000$ g/mol) was firstly modified with excess 1,6-diisocyanatohexane (HDI) at 80 °C for 1.5 h in DMAc solvent to obtain a prepolymer. In the following, HMA and 1,4-butanediol (BDO) (dissolved in DMAc solvent) were both used as the chain

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