Full Length Article

Self-healing polyurethane based on ditelluride bonds

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A B S T R A C T

Ditelluride bonds have been reported as dynamic covalent bonds which could undergo reversible formation and cleavage at room-temperature. In this work, a novel self-healing ditelluride-containing polyurethane was synthesized by incorporating ditelluride bond into its main chain. Base on the dynamic nature of ditelluride bonds, this polyurethane could self-heal in darkness at room temperature without external intervention. The study on the exchange mechanism revealed that the reversible exchange of ditelluride bonds and the intermolecular hydrogen bonding were the two main factors that responsible for the self-healing behavior of this polyurethane. The ditelluride content and chain mobility of the polymer have a significant effect on its self-healing property. The unique non-intervention self-healing properties and wild applicability makes this polymers ideal for environment friendly smart systems.

1. Introduction

Self-healing materials that can recover their structures and properties after damage have attracted more and more interest in recent years [1–6]. Supramolecular chemistry and dynamic covalent chemistry are the two main strategies to fabricate self-healing materials [7,8]. For supramolecular systems, the non-covalent interactions include hydrogen bonding [9], host-guest interactions [10,11], π-π stacking [12] and mental-ion binding interactions [13], which have been applied to synthesize self-healing gels and self-healing bulk materials [14,15].

Apart from the supramolecular chemistry, various self-healing polymers have been developed base on reversible dynamic covalent bonds which include imine bonds [16], disulfide bonds [17,18], Diels-Alder (DA) reaction [19,20], reversible radical reactions [21] and so on. For example, many thermally self-healing polymers have been designed base on the reversible Diels-Alder reaction at different temperature [22–24]. Zhou Qiao Lei et al. [25], reported a novel crosslinked polymer with self-healing and remolding properties as a result of the dynamic exchange of aromatic Schiff based bonds. Guohua Deng and co-workers [26] presented an approach to design a self-healing gels base on the reversible formation and cleavage of acylhydrazone bonds under acid condition.

Among these dynamic covalent bonds, disulfide bonds have been gained more attention for its diverse stimulus-response behaviors. A number of dynamic covalent polymers have been designed based on dynamic thiol/disulfide exchange [27–30]. For instance, Zhou Qiao Lei [31] synthesized a room-temperature self-healable cross-linked

polysulfides based on the dynamic exchange of disulfide bonds in the present of catalyst. Wei Min Xu et al. [32] fabricated a crosslinked polyurethane carrying disulfide bonds in the main chain, which could repeatedly healed in the sun. In comparison with disulfide bonds, diselenide bonds are more dynamic and the diselenide metathesis can happen under much mider condition [33]. Based on this concept, a self-healing diselenide-containing polyurethane elastomer was designed as the result of visible-light-triggered reversible exchange of diselenide bonds [34]. Although various self-healing systems have been developed base on dynamic covalent chemistry, an external intervention was required for the majority of those systems to trigger the dynamic exchange reaction, which limit the application of those self-healing materials. So it is necessary to develop a system which have the ability to self-heal under mild condition without external intervention.

According to the literature [35], ditelluride bonds possess a lowest bond energy (126 kJ mol^{-1}) in comparison with disulfide bonds (240 kJ mol^{-1}) and diselenide bonds (172 kJ mol^{-1}), which suggested that ditelluride bonds might be the most dynamic. Actually the ditelluride exchange reaction could carry out spontaneously at room temperature [36], which avoid the harmful from external intervention. However, to the best of our knowledge, self-healing polymers base on the reversible ditellurite bonds were rarely reported.

Herein a novel ditelluride compound bis (2-hydroxyethyl)-ditelluride (HOC$_2$H$_4$Te)$_2$ was synthesized and characterized. Its dynamic properties were explored by ^{13}C NMR, ^{1}H NMR and ^{125}Te NMR spectrum through a model ditelluride exchange reaction. The exchange reaction could proceed in the dark at room temperature without

external stimuli and reach equilibrium state immediately. The ditelluride containing polyurethane (PUTeTe) was then synthesized by using $(HOC_2H_4Te)_2$ as the chain extender and its dynamic properties in solution was studied by GPC. The self-healing properties of PUTeTe was investigated and the effect of ditelluride content and chain mobility on its self-healing ability were also studied.

2. Experimental Section

2.1. Materials

Telluride powder (Te, 99%), 4,4-Diphenyl-methane-diisocyanate (MDI, 99%), 2-bromoethanol $(HOC_2H_4Br, 97\%)$, sodium borohydride $(NaBH_4, 98\%)$ and phenyl ditelluride $((PhTe)_2, 98\%)$ were purchased from Aladdin and used without further purification. Poly(ethylene glycol) (PEG, Mn = 1000 Da, purity: 99.99%) and Poly(tetramethylene glycol) (PTMG, Mn = 1000 Da, purity: 99.99%) were bought from Sigma-Aldrich. 1,4-butylene glycol (BDO, 98%) and N,N-dimethylformamide (DMF) were dried over CaH_2 and distilled under vacuum prior to use. All other reagents were obtained from Shanghai Lingfeng Chemical Reagent and used as received.

2.2. Instruments

All ^1H NMR (400 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Advance spectrometer using TMS as the internal standard. ^{125}Te-NMR spectra were performed by a Bruker Advance 600 (189 MHz) spectrometer using phenyl ditelluride as the external standard. Gel permeation chromatography (PL-GPC 50 Plus, Varian) was applied to analyze the molecular weight distributions of polymers at 35 °C with N,N-dimethylformamide (DMF) as the mobile phase at a flow rate of $1 \, mLmin^{-1}$. The mechanical properties of polymers were determined by a TA instrument Q800 DMA applying controlled strain tension mode with ramp force rate of $0.1 \, N \, min^{-1}$ till the samples yielded. Differential Scanning Calorimetry (DSC) analysis was performed on a TA Instruments modulated DSC 2010 analyzers under nitrogen atmosphere. Each sample (3–5 mg) was first heated from −100 to 100 °C, followed by cooling to −100 °C to remove the thermal history and then heated to 100 °C at a rate of $10 \, °C \, min^{-1}$. Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet 5700 spectrometer Nicolet spectrometer. Raman spectroscopy was performed on a laser Raman spectrometer, utilizing 785 nm line of a laser.

2.3. Preparation of di-(1-hydroxyethyl) ditelluride $((HOC_2H_4Te)_2)$

Tellurium (7.66 g, 60 mmol), sodium borohydride (2.27 g, 60 mmol) and 150 mL of distilled water were added into a 500 mL round bottom flask. The mixture was stirred at 40 °C for 3 h with argon protection. After cooling down to ambient temperature, a transparent purplish red aqueous solution was obtained. Then 2-bromoethanol (7.50 g, 60 mmol) in deaerated THF (100 mL) was added into the above solution with argon protection and stirred at 45 °C for another 5 h. The mixture solution was extracted with dichloromethane and dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (ethyl acetate: dichloromethane = 1:1 v/v). The purplish red di-(1-hydroxyethyl) ditelluride $((HOC_2H_4Te)_2)$ was obtained with a yield of 63%. ^1H NMR (400 MHZ, $CDCl_3$) δ (ppm): 3.88 (4H, t, $HOCH_2$), 3.12 (4H, t, $TeTeCH_2$) and 2.12 ppm (2H, s, $HOCH_2$). ^{13}C NMR (125 MHZ, $CDCl_3$) δ (ppm): 64.61 and 8.21. ^{125}Te NMR (189 MHZ, $CDCl_3$) δ (ppm): 307.2.

2.4. Model ditelluride exchange experiment

A typical ditelluride exchange experiment was carried out by mixing $(HOC_2H_4Te)_2$ (6.9 mg, 0.02 mmol) and $(PhTe)_2$ (8.2 mg, 0.02 mmol) in $CDCl_3$ (0.5 mL) at room temperature in darkness. After that, the mixture

solution was measured via ^1H NMR, ^{13}C NMR and ^{125}Te-NMR spectroscopy in situ. The diagnostic peaks assigned to different compounds and the composition of the mixture solution were investigated.

2.5. Preparation of ditelluride-containing polyurethane and its control

The ditelluride-containing polyurethane with different composition were synthesized in the classical two steps using $(HOC_2H_4Te)_2$ as chain extender. Taking the preparation of PUTeTe-2251 as an example, PTMG (1 g, 1 mmol) and PEG (1 g, 1 mmol) were fed into a 25 mL flame-dried Schlenk flask equipped with a magnetic bar. The flask was then degassed under vacuum at 80 °C for 6 h to remove the moisture completely. After cold down to 60 °C, MDI (0.625 g, 2.5 mmol) was added into the flask under dry argon flow and stirred for 1.5 h to prepare the prepolymer. Then $(HOC_2H_4Te)_2$ (0.172 g, 0.5 mmol) with 4 mL DMF were added to the flask and stirred for another 3 h. The red solid was obtained by precipitation into diethyl ether and dried under vacuum at 30 °C for 4 h (Yield: 2.65 g, 95%). During the polymerization, the ratio of reactants were tuned to synthesize polyurethanes with different composition. For the convenience of self-healing mechanism analysis, a control polyurethane (PUB-2251) excluding ditelluride bond was prepared following the synthesis procedures as described above, except that $(HOC_2H_4Te)_2$ (0.172 g, 0.5 mmol) was replaced with BDO (0.045 g, 0.5 mmol).

2.6. Dynamic properties of ditelluride-containing polyurethane

A model ditelluride exchange reaction was performed to investigate the dynamic properties of ditelluride-containing polyurethane. Typically, PUTeTe-2251 (0.5 g) was dissolved in DMF (5 mL) and excess $(HOC_2H_4Te)_2$ was added into the solution. The mixture solution was stirred at room temperature in the darkness for 12 h. After reaction, the exchange product (PUTeTe-2251′) was isolated by precipitating in diethyl ether and dried under vacuum at 30 °C for 4 h. The number-average molecular weight of PUTeTe-2251 and PUTeTe-2251′ were analysis. Similarly, the dynamic property of the control material (PUB-2251, which does not contain ditelluride bond) was investigated following the same procedures.

2.7. Self-healing property evaluation

The self-healing experiments were performed by preparing tensile bars (30*10*1 mm), cutting these bars into two pieces and attaching them together in the fresh crack surfaces. These bars were subsequently healed in dark at 20 °C for a given time. Tensile tests were performed on those virgin and healed bars to quantitatively evaluate their self-healing properties.

3. Result and discussion

3.1. Dynamic properties of ditelluride bonds

The di-(1-hydroxypropyl) ditelluride $((HOC_2H_4Te)_2)$ was successfully synthesized via a two-step procedure (Scheme S1). Its structure was confirmed by ^1H NMR, ^{13}C NMR and ^{125}Te-NMR spectra (Figs. S1–S3). Although exchange of ditelluride bonds has been found to occur at room temperature, the dynamic nature of it relate to ditelluride compounds. In order to reveal the reversible property of ditelluride bonds in $(HOC_2H_4Te)_2$, a model mixture of small molecules $((PhTe)_2$ and $(HOC_2H_4Te)_2)$ was studied. The exchange reaction equation between $(PhTe)_2$ and $(HOC_2H_4Te)_2$ was depicted in Fig. 1a, after exchange an asymmetric ditelluride product $(HOC_2H_4TeTePh)$ containing hydroxyl and phenyl groups was formed in equilibrium state. The exchange reaction was modified by ^1H NMR, ^{13}C NMR and ^{125}Te NMR spectra. After equmolar of $(PhTe)_2$ and $(HOC_2H_4Te)_2$ mixing in $CDCl_3$, a new peak at 3.33 ppm which belong to the $TeCH_2$ proton in