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Chemical recycling of poly(thiourethane) thermosets enabled by dynamic thiourethane bonds†

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Recycling of polyurethanes is largely infeasible due to the harsh reprocessing conditions and associated risks of side reactions and degradation whereas polymer networks incorporating dynamic covalent bonds represent an attractive approach to the design of recyclable materials. Here, we report findings on the dynamic nature of thiourethanes, and their application as a new class of recyclable analogs of urethane materials. A series of small molecule experiments was initially conducted to determine the equilibrium constant and exchange reaction kinetic constant for the thiol–isocyanate reaction. Furthermore, incorporating those thiourethane moieties into a cross-linked network resulted in thermoset materials that are readily depolymerized to liquid oligomers. The resultant oligomers can be re-crosslinked to thiourethanes without any loss of performance nor change in mechanical properties (peak stress of 25 MPa with max strain of 200%). Moreover, the recycled thiol oligomers from thiourethane network polymers could potentially be transformed into other materials with mechanical properties that exceed those of the initial, pristine thiourethane materials. Overall, the ease with which these polythiourethanes are polymerized, recycled and reformulated gives a new direction and hope in the design of sustainable polymers.

Introduction

Polyurethanes are major consumer plastic materials with an estimated global market size of USD 91 billion by 2026, ranking 7th in global plastics production with an annual production of 27 million tons in 2015.[1] In particular, due to their superior mechanical properties, polyurethane polymers are ubiquitous and have been extensively used for a wide range of applications.[2] However, to date, recycling of polyurethanes, especially crosslinked polyurethane networks, is an impractical, low value business due to numerous difficulties associated with reprocessing and/or repurposing these materials. Less than 20% of polyurethanes, mainly polyurethane thermoplastics, are recycled by rebonding, adhesive pressing, and glycolysis.[3]

The dissociative reversion of carbamate bonds to isocyanates and alcohols has been studied since around the same time that polyurethanes were first synthesized back in the 1930s.[4] This dissociative reaction occurs at high temperatures (~200 °C), which generally leads to deleterious side reactions.[5] Interestingly, incorporating dynamic covalent bonds into polymer networks is an attractive strategy for the design of recyclable materials. Unfortunately, recycling of polyurethanes is still an infeasible process, at least through the transcarbamate reaction.[6] To date, most recyclable and reprocessable polyurethane systems rely on remolding processes, which generally require high temperature,[7,8] metal catalysts,[9] and suffer from a reduction in mechanical properties of the recycled materials relative to the pristine materials.[10] In order to overcome these limitations, many attempts have been undertaken including appropriate selection of catalysts,[11] insertion of other dynamic chemistries,[11,12] and alternative polymerization methods.[6,13,14]

In contrast to the remolding process, chemical recycling of vitrimers focuses on converting or depolymerizing networks to soluble monomers or oligomers under mild conditions. The resultant monomers or oligomers can be purified, separated from composites and nanoparticles, and ultimately would lead to resynthesized materials with properties identical to the virgin material. For example, Christensen *et al.* demonstrated a closed-loop recycling system that enables upcycling of poly(diketoenamine) thermoset at ambient temperature.[15] Wang *et al.* formed recyclable photopolymers based on the reversibility and reactions of the thioester bond.[16,17] Furthermore, an electronic skin could be fully recycled to monomers and silver

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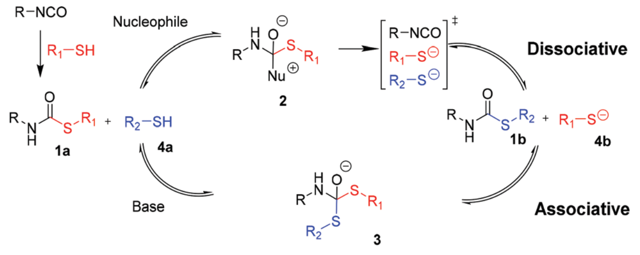
nanoparticles with the assistance of polyimine dynamic covalent chemistry.[18] Additionally, not only limited by obtaining material with the same mechanical properties, chemical recycling of vitrimers also offers re-formulation opportunities for achieving higher value materials. Currently, few successful examples of chemical recycling have been reported for polyurethane networks except for experiments involving solvolysis of the networks without further implementation of recovered monomers/or oligomers.[6,19]

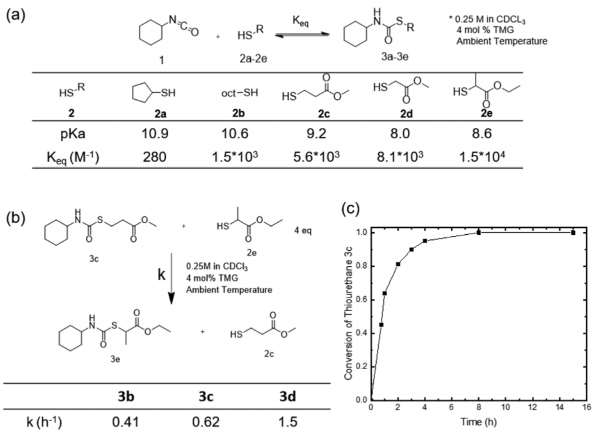
As one of the reactions in the thiol-X click paradigm, the thiol–isocyanate reaction has been known for its rapid reaction kinetics, minimal by-product formation, and mild reaction conditions.[20] Compared with polyurethane networks, thiourethane networks generally show more homogeneous topology due to high reaction efficiency.[21] Although there are few limitations of using thiol monomers for polythiourethanes such as high cost and unpleasant odor, thiourethane network can provides similar mechanical properties as urethanes while enabling recycling and reuse would be significantly hindered in urethanes. With a similar backbone structure, the urethane and thiourethane linkages provide nearly identical extent of hydrogen bonding and therefore similar physical and mechanical properties.[22] Moreover, one distinct advantage of thiourethane networks is the dynamic character of the thiourethane bond as compared to the urethane bond. As recently reported, Li *et al.* demonstrated the dual associative and dissociative mechanisms of the thiourethane exchange reaction. It was shown that the dynamic nature of the thiourethane moieties enables designing recyclable thiourethane networks with full recovery of cross-link density and tensile properties at elevated temperature.[19] Wen *et al.* further investigated the detailed mechanism of the thiourethane bond dynamics based on the choice of strong base or strong nucleophile as catalysts (Scheme 1).[23] The associative pathway involves the attack of a thiolate anion (**4a**) on the carbonyl carbon of (**3**) and regeneration of a thiocarbamate (**1b**) and thiolate anion (**4b**) in the presence of a strong base. With a strong nucleophile, the thiourethane exchange reaction goes through a dissociative pathway which involves the attack of a nucleophile on the carbonyl group of (**2**) and regeneration of the thiolate anion and isocyanate. Furthermore, the associative mechanism has been utilized in designing reprocessable poly(thiourethane) thermosets with self-welding ability at higher processing temperature (>160 °C).[24,25] Herein, to extend further the potential for sustainable recyclable thiourethane networks, the chemical recycling strategy of the thiourethane thermosets is presented with a goal to address the arising challenges for manufacturing, material performance, recycling and re-formulation. Specifically, the thiourethane network with only minimal synthetic challenges are depolymerized to liquid oligomers at ambient temperature. The recycled oligomers not only are repolymerizable to polythiourethanes without any noticeable sacrifice in mechanical performance but also can be reformulated as a photopolymerizable resin for additive manufacturing by means of rapid prototyping. A 3D printed globe was printed with recycled oligomer.

Results

To evaluate the dynamic nature of thiourethane bonds, a series of small molecule experiments was initially conducted to determine the equilibrium constants for the thiourethane reaction based on several different functional groups (Fig. 1). Five monothiols, namely cyclopentanethiol, octanethiol, methyl 3-mercaptopriopionate, methyl thioglycolate, and ethyl 2-mercaptopropionate, were utilized with significant variations in their pK_a values. A strong base, 1,1,3,3-tetramethylguanidine (TMG), was used as the catalyst for this model compound study. As expected, the equilibrium constant is highly dependent on the structure of the thiol. Generally, the acidities of thiols increase in the row from **2a** to **2d** along with the corresponding increasing trend for the thiol–isocyanate equilibrium constant (Fig. 1a, ^{1}H NMR spectrum in ESI Fig. S1–S5†). Under the basic catalysis process, a more acidic thiol is kinetically more reactive and thermodynamically less stable, thus leading to a higher equilibrium constant. One thing worth pointing out is that the exceptionally high equilibrium constant of for



Scheme 1 A general scheme for the thiourethane dynamic chemistry. Associative mechanism through basic catalysis and dissociative mechanism through nucleophilic catalysis.



2	2a	2b	2c	2d	2e
pKa	10.9	10.6	9.2	8.0	8.6
K_{eq} (M^{-1})	280	1.5*10^3	5.6*10^3	8.1*10^3	1.5*10^4

	3b	3c	3d
k (h^{-1})	0.41	0.62	1.5

Fig. 1 (a) Equilibrium constant, association rate constant, and dissociation rate constant of thiourethane bonds. (b) Exchange reaction between **3c** and a 4-fold excess of **2e**. (c) Conversion-time dependence of thiourethane **3c**.

the thiourethane **3e** is likely caused by the contribution of the 7-carbon ring formation including the hydrogen bond, which thermodynamically stabilizes the corresponding thiourethane structure as compared to the reactants.

The exchange reaction kinetics of the thiourethane bond were further evaluated by subjecting thiourethanes **3b–3d** to a 4-fold excess of thiol **2e** to obtain a pseudo-first order reaction in the early stage of the reaction. Since a large excess of thiolate anion was present in the system, the reaction would preferably go through an associative pathway instead of a dissociative pathway. The reaction was conducted at ambient temperature in the presence of 4 mol% TMG as the catalyst. All three thiourethane monomers undergo the exchange reaction and form a new thiourethane monomer with **2e** at ambient temperature (^{1}H NMR spectrums in Fig. S6–S9†). Fig. 1c shows a representative conversion of thiourethane **3c** *vs.* time. Interestingly, thiourethanes derived from more acidic thiols were found to undergo exchange reactions faster than the ones with higher pK_a, *i.e.* less acidic. The thiol anions formed by more acidic thiols are relatively less electronic dense. Therefore, the resultant thiocarbamates are thermodynamically less stable, which leads to a faster exchange reaction. To assess further the kinetics of the thiourethane exchange reaction, the exchange reaction with thiourethane **3b** and **2e** was conducted at varying temperatures (25 °C, 40 °C, 55 °C, and 65 °C). An activation energy of 48 ± 4 kJ M^{-1} was determined for the exchange reaction based on the best fit value in a typical Arrhenius' plot (ESI Fig. S7†). For comparison, this value is 90 kJ M^{-1} lower than that of urethane exchange in the presence of DBTDL as a catalyst[8] and similar with that of vinylogous ureas and vinylogous urethanes.[14,26] This calculated activation energy is much lower than that in a thiourethane polymer network as reported previously,[19,23] which is consistent with the Semenov-Rubinstein model of dynamic cross-linked networks.[27]

With this dynamic chemistry in hand, thiourethane bonds were incorporated into a thermoset network with the goal of creating a recyclable thermoset material. With recent progress in the development of thermally-latent base catalysts, temporal control of the thiol–isocyanate reaction can be achieved through the use of a thermal-latent base,[28] or an acid/nucleophile co-initiator,[29] or photolatent base catalyst.[30] For the simplicity of this work, a thermally-latent base 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) was used to initiate the thiol–isocyanate reaction at elevated temperatures. As shown in Fig. 2a, a thiourethane thermoset network was fabricated from a commercially available trithiol (ethoxylated trimethylolpropane tri (3-mercaptopropionate), ETTMP700) and diisocyanate (4,4′-methylenebis(cyclohexyl isocyanate), CHDI) in the presence of a thermally-latent base catalyst, *i.e.*, TEMPO, at 80 °C for 6 hours. The thiourethane linkage in each of its repeating unit is stable in neutral and basic conditions. Although the resultant thiourethane networks can be depolymerized by different thiol monomers with varied functionality, the same trithiol, ETTMP700, was used in the depolymerization process to maintain the same crosslink density and mechanical properties for the reclaimed thiourethane network. Upon addition of excess trithiol, 9 equivalencies to the thiol functional monomers, and 4 wt% of strong base TMG, the thiourethane network was facilely depolymerized to liquid oligomers within 4 hours at ambient temperature in acetone. Based on the Flory-Stockmayer equation, the critical gelation point for a step-growth polymerization system can be calculated as $p = \sqrt{\dfrac{1}{r(f_a - 1)(f_b - 1)}}$, whereas f is the functionality of thiol (f = 3) and isocyanate monomers (f = 2). Therefore, this network polymer can be depolymerized when the excess thiol functionalities are higher than one molar equivalent of the isocyanate functional groups (*i.e.*, the stoichiometric ratio of isocyanate to thiol functional group concentration, r, need to be lower than 0.5 to keep critical gelation point conversion, p, above 1). To test this hypothesis, we designed a series of formulations with 0.5 (r = 0.67), 3 (r = 0.25), 5 (r = 0.17), and 9 (r = 0.1) molar equivalents excess of thiol monomers. As expected, all polymer networks depolymerized to liquid oligomers except for the one with 0.5 molar equivalents excess of thiol monomers. As confirmed by ^{1}H NMR, all of the depolymerized oligomers have similar backbone structures as the starting materials (ESI Fig. S10†). Moreover, the lower thiol loading results in a more viscous oligomer solution due to a higher molecular weight and more extensive hydrogen bonding (ESI Fig. S12†). Therefore, throughout the remainder of this study only nine molar equivalent excess of thiol monomers for the depolymerization process was used to avoid handling viscous liquids.

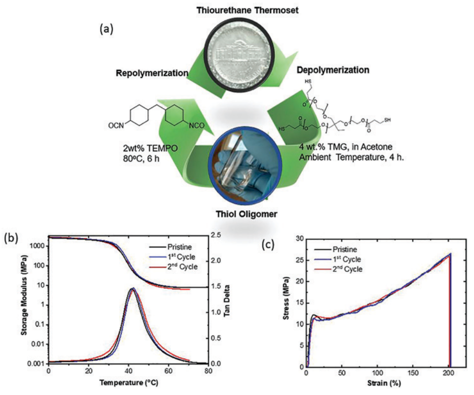


Fig. 2 (a) Reaction scheme for depolymerization and repolymerization process of thermal initiated thiourethane thermosets. (b) Dynamic mechanical analysis of pristine and reclaimed thiourethane networks. (c) Tensile stress–strain curves of pristine and recycled thiourethane thermosets.

Followed by a simple acid wash procedure to wash out the strong base catalysts, the resultant oligomers were recrosslinked to a thiourethane network in the presence of 2 wt% TEMPO and a stoichiometric ratio of diisocyanate at 80 °C for 6 hours to obtain a reclaimed polythiourethane network (Fig. 2a). Two cycles of this operation were conducted without any noticeable loss of properties or thermal performance. As shown in Fig. 2b and c, the thermomechanical properties showed consistent behaviour in terms of glass transition temperature and storage modulus between the pristine and regenerated polymer networks. In addition, a universal tensile test shows both pristine and reclaimed polymer break at ~200% strain with a max stress of 25 MPa. In addition, swelling tests and thermogravimetric analysis (TGA) further confirmed the consistent material performance between the pristine and reclaimed polymer networks as presented in the ESI (S14, Tables S1 and S2†). Due to the step-growth nature of the thiol–isocyanate polymerization, varied chain lengths of trithiol can be facilely incorporated into the thiourethane network which facilitates tunability of mechanical properties without sacrificing the materials' recyclability. For example, incorporation of TMPTMP into polythiourethane networks leads to stiffer, more glassy networks (T_g = 100 °C) whereas incorporation of a long chain trithiol, ETTMP1300, results in much softer and rubbery materials (T_g = −10 °C) (ESI Fig. S11†). Similarly, this recyclable thiourethane network is readily extended to a broad range of polymer formulations with a wide range of commercially available isocycanate structures. The structure of the diisocyanate had a significant impact on the final material's mechanical properties. As shown in Fig. S13,† CHDI and TDI exhibited much higher Young's modulus and toughness compared with XDI and HXMDI due to the rigid backbone of the respective monomers. Those superior mechanical responses are comparable with commercially available polyurethane networks (Smooth-Cast® 57D and PMC®-790),[31] while enabling recycling and reuse nor possible in urethanes. Nevertheless, with addition of excess trithiol and TMG, the crosslinked structure was entirely dissipated within 4 hours in acetone. Notably, due to its sterically hindered and packed structure, the thiourethane network made with HXMDI required harsher conditions (10 mol% TMG) to depolymerize at ambient temperature. As exemplified above, this study brings evidence that the thiourethane exchange reaction is applicable to a variety of isocyanate structures, both aromatic and aliphatic isocyanate monomers.

The benefits of chemical recycling of polythiourethane networks are not limited to the reclamation of the polythiourethanes themselves but may lead to more diverse materials through appropriate re-formulation of the recycled thiol oligomers. Thiol functional monomers have been known as the reactant for the thiol–click reaction family such as thiol–ene, thiol–Michael, and thiol–epoxy reactions. Among those, the radical-mediated thiol–ene photopolymerization has been introduced in a wide range of applications such as dental materials,[32] surface modification,[20] and additive manufacturing.[33] Hence, the recycled thiol oligomers from the original thiourethane networks were further re-formulated as a resin suitable for additive manufacturing (3D printing). More specifically, a stoichiometric ratio of recycled thiol oligomers and triallyl monomer, TATATO, were mixed with a catalytic amount of a radical initiator, Irgacure 2022, and an inhibitor, pyrogallol. As shown in Fig. 3b, the thiol–ene photopolymerization occurred rapidly and reached quantitative conversion within 2 min irradiation of 405 nm light with a light intensity of 0.4 mW cm^{-2}, which is consistent with the light source of a masked SLA 3D printer, Prusa SL1. As shown in Fig. 3c, a 3D printed structure (globe with a recycle bin) with high precision was fabricated. Hence, with this chemical strategy of recycling of polythiourethanes, the facile recovery of thiol oligomers enables reuse for preparation of new polymers with the same or even improved mechanical properties and performance, thus maximizing the value of the spent materials.

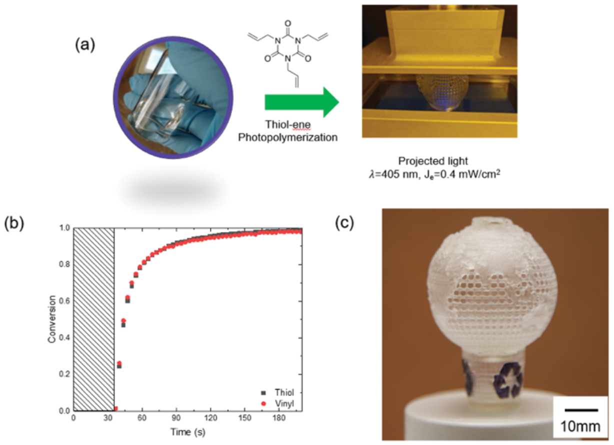


Fig. 3 (a) A scheme of 3D printing process with recycled thiol oligomers. (b) Reaction kinetic profiles of the thiol-ene photopolymerization. The sample was irradiated with 0.4 mW cm^{-2} 405 nm wavelength at ambient temperature. (c) A 3D printed globe made by recycled thiol oligomers and TATATO.

Conclusions

Herein, model experiments were performed to evaluate the dynamic nature of the thiourethane bond. It was shown that the less acidic thiol is less thermodynamically favored during the thiourethane formation process due to having a more stable thiolate anion. For the exchange reaction under basic condition, the thiourethane bond with a more acidic thiol shows faster exchange kinetics due to a less stable thiourethane bond. A series of recyclable thiourethane thermosets was formed by thiol–isocyanate polymerizations with great tunability and variability of the mechanochemical behavior as dictated by the structures of the reactive monomers. With an excess of thiol and strong base, the polymer network is readily depolymerized into liquid oligomers which are readily repolymerized to polythiourethane networks with nearly identical mechanical properties. Furthermore, the recycled oligomers were found to be suitable for construction of other types of networks such as thiol–ene photopolymer networks which were implemented in additive manufacturing. Overall, the chemical recycling strategy of polythiourethane materials presented in this work may advance global sustainability goals and could be applied to other dynamic covalent materials to increase the scope of recyclable thermosets.

Conflicts of interest

There are no conflicts to declare.

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