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A weak but inert hindered urethane bond for high-performance dynamic polyurethane polymers

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ABSTRACT

Covalent adaptable networks (CANs), which share the properties of both thermosets and thermoplastics at the same time, are desirable for many applications. Introducing bulky substituents is a feasible way to design dynamic covalent bonds for constructing CANs, as evidenced by the successful implementation in CANs based on hindered urea bonds (HUBs). However, the dynamicity induced by introducing bulky substituents always come with low bond energy, resulting in low mechanical strength and poor stability of the CANs. Herein, we designed a novel hindered urethane bond, which is weak in thermodynamic (K_{eq} = 1701.23 L/mol at 25 °C) and inert in kinetic at low temperature, but stable in thermodynamic ($K_{eq} = 1.54 \times 10^4$ L/mol at 100 °C) and active in kinetic at high temperature (k_{-1} = 0.105 h^{-1} at 80 °C and 0.315 h^{-1} at 120 °C). As a result, the polyurethane based on it exhibits high mechanical properties (with Youngs' modulus of 1011 ± 29 MPa and flexible modulus reached 1833 ± 50 MPa) and excellent reversibility (can be reprocessed at 60 °C under 100 kPa in 30 min and completely healed at 40 °C in 10 min). Moreover, unlike to many CANs based on hindered urea bonds, our dynamic polyurethanes are highly stable in humid environment or even water solutions due to the slow hydrolysis kinetics. Such high-performance dynamic polyurethane polymers are attractive for many applications.

Traditional thermoset polymers have been widely used in our daily life. These materials play a significant role in medical [1–3], transportation [4], construction [5,6], electronic engineering [7–9] and so on, due to their good physical and chemical properties [10]. However, these materials are hard to be reprocessed or degraded owning to the strong and irreversible crosslinked structures [11,12]. After being discarded, they will cause great waste of resources and severe pollution of environment [13,14]. In 2002, Wudl *et al.* firstly discovered the covalent adaptable networks (CANs) [15], in which the introduced dynamic bonds in crosslinked polymers can be exchanged efficiently and reliably [16]. Thus, such CANs can achieve fast topology rearrangements due to dissociation of dynamic bonds and decrease in connectivity at high temperature, thus behave like thermoplastic materials [17,18]. Meanwhile, the dynamic bonds are formed again upon cooling [19–24], so the connectivity will reach the same extent as the original one. Therefore, the thermoset-like robustness and stabilities can be preserved or reinstalled [25].

Among the various strategies for constructing CANs, introducing bulky substituents to design dynamic covalent bonds is advantageous as it does not require harsh reaction conditions (*i.e.*, basic or acidic solutions and/or high temperatures) or catalysts to initiate the bond exchange process [24–28]. In 2014, Cheng *et al.* first reported the dynamic polyurea thermosets based on hindered urea bonds (HUBs) [29]. The introduction of bulky substituents on the nitrogen atom weakened the planarity of the amide bond, which in turn reduced the stability of the urea bonds and resulted in the dissociation of isocyanate and amine under mild conditions. The poly(urea/urethane)s based on HUBs exhibited excellent self-healing, recycling, and shape-memory properties. Since then, a lot of CANs based on HUBs have been designed and synthesized [30–32]. However, the strategy of introducing bulky substituents to design dynamic covalent bonds is still limited to polyureas. It is desirable to design more dynamic commodity polymers with hindered bonds. Moreover, the dynamicity induced by introducing bulky substituents always come with low bond energy, resulting in low mechanical strength and poor stability of the CANs. It is a great challenge to design hindered bonds with both good dynamicity and high environmental stability [33–35].

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Chemical reactions can be controlled by both thermodynamics and kinetics. A weak bond breaks easily due to its low dissociation energy, thus leading to poor stability. However, if the dissociation process is very slow, the bond can still be stable enough. For example, nanoparticles have the tendency to aggregate, but some nanoparticles can be stored for a long time due to kinetic stability; diamond is kinetically stable although the conversion from diamond to graphite is thermodynamically favorable; some kinetic inert coordination complexes (such as $[Co(NH_3)_4]^{3+}$) decomposes very slowly in spite that they are thermodynamically unstable. We envisage that designing a weak but kinetically stable bond can address the tradeoff problem between dynamicity and stability. According to our previous studies [36], crosslinking low-molecular-weight monomers with abundant weak bonds can lead to strong and dynamic materials. Meanwhile, if the weak bonds are kinetically inert, sufficient environmental stability can be expected.

Herein, by utilizing *tert*–butyl as the hinderance group, we designed and synthesized a novel hindered urethane bond (HUrB), which shows good kinetic stability (with a counter reaction rate constant of 1.41×10^{-2} h^{-1}) at room temperature while the bonding constant is quite small (1.70×10^3 L/mol). Meanwhile, when temperature is getting higher, the bonding constant and reaction rate constant increase simultaneously. The bonding constant reached 10^4 L/mol and the reaction rate constant of counter reaction reached 5.46×10^{-2} h^{-1} at 60 °C. Therefore, the new hindered urethane bond is weak in thermodynamic and inert in kinetic at low temperature, but stable in thermodynamic and active in kinetic at high temperature. Polyurethane based on such bond (PHUr) exhibits high mechanical strength (with Youngs' modulus of 1011 ± 29 MPa), excellent reversibility (can be reprocessed at 60 °C under 100 kPa in 30 min and completely healed at 40 °C in 10 min), and excellent environmental stability (nearly no dissociation in humid environment or even water solutions, 2.48% of the maximum water swelling capacity in 30 days). Such high-performance dynamic polyurethane polymers are attractive for many applications.

According to Arrhenius equation ($\ln k = -E_a/(RT) + C$), the reaction rate constants are determined by the temperature and apparent activation energies (E_a) [37]. When the temperature is fixed, E_a become the dominant factor. Therefore, in order to design an inert bond, we need to select bonds with high E_a. Base on this consideration, we choose urethane bonds for our investigation. According to many experimental or theoretical studies, the urethane bond presents a weak C–O bond with a quite high activation energy of dissociation (in the range of 100–130 kJ/mol) [38,39]. The activation energies reported for pure vinylogous urethane vitrimers (68–149 kJ/mol) are significantly higher than those for pure vinylogous urea vitrimers (49–53 kJ/mol) [40]. Moreover, polyurethane has been widely used in almost all aspects of our daily life since it was first discovered by the German scientist Otto Bayer *et al.* in 1937 [41,42]. It is of great importance to develop polyurethane polymers that show high mechanical strength, good chemical stability and dynamic properties [43].

Alcohols with different bulkiness (DPhOH, PhOH and ^{t}BuOH) were selected in our study (Fig. 1a). Products between these alcohols and isocyanate were denoted as DPh-urethane, pH-urethane and ^{t}Bu-urethane, respectively. We firstly examined the equilibrium constants of these reactions through ^{1}H NMR spectra with an indirect method [24,44]. Due to the low reactivity of alcohol and high steric hindrance, the equilibrium constants of DPh-urethane (Fig. 1b, 18.50 L/mol), pH-urethane (Fig. S1 in Supporting informa-

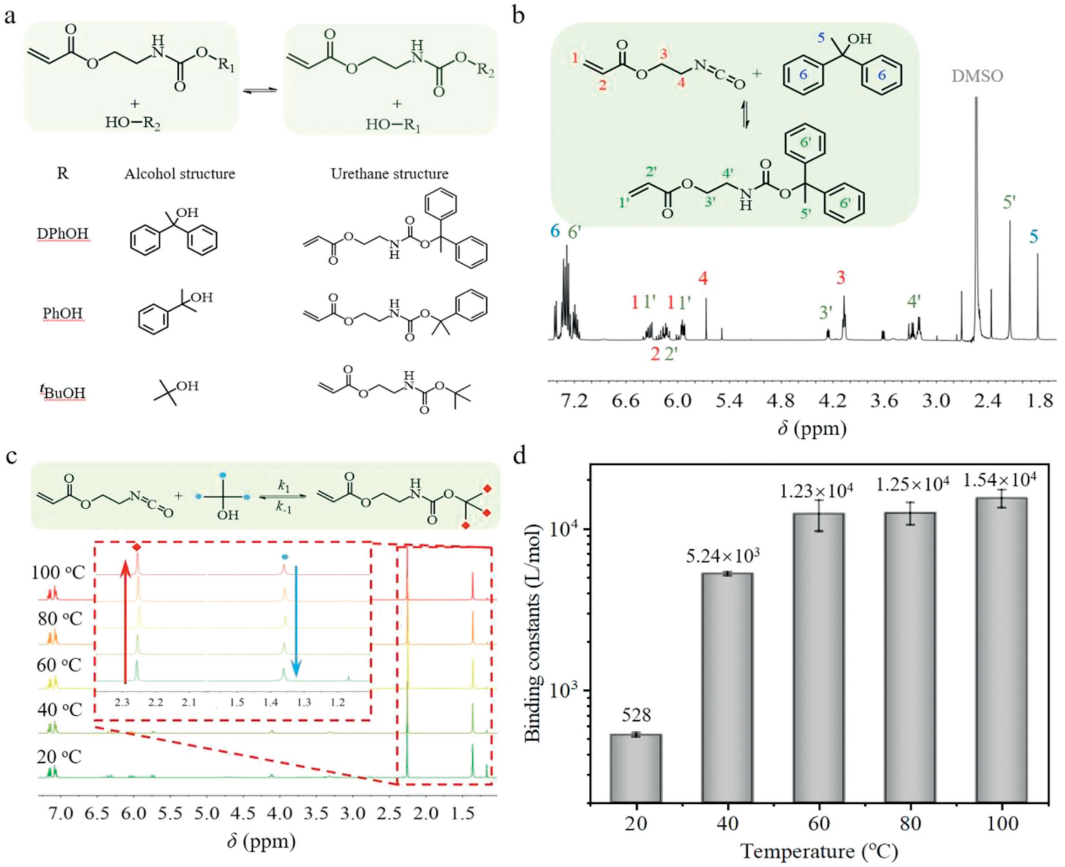

Fig. 1. (a) Dynamic exchange reactions of model molecules containing HUrBs, and the structures of alcohols and urethanes. (b) ^{1}H NMR spectrum of reversible reaction between 2-isocyanatoethyl acrylate and DPhOH. (c) Temperature resolved ^{1}H NMR spectra of ^{t}Bu-urethane. (d) The bonding constants for ^{t}Bu-urethane at different temperatures.

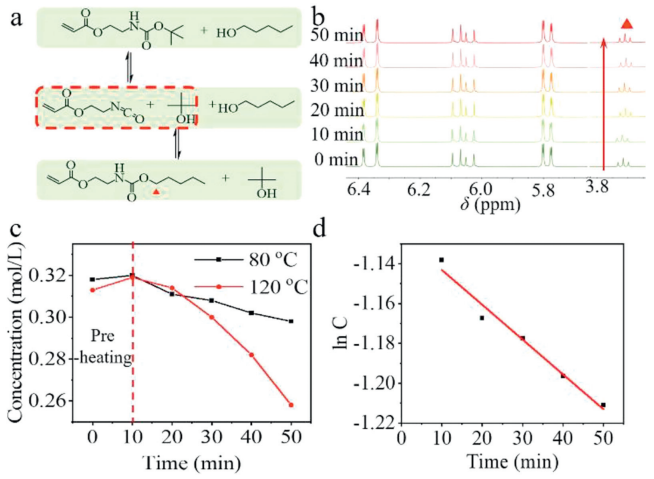

Fig. 2. Exchange reaction of ^{t}Bu-urethane and *n*-pentanol (*n*-POH). (b) Time resolved ^{1}H NMR of the exchange reaction at 120 °C (393 K). (c) The concentrations of ^{t}Bu-urethane at 80 °C (353 K) and 120 °C (393 K). (d) Time resolved concentrations and Arrhenius curve of ^{t}Bu-urethane at 80 °C (353 K).

tion, 313.40 L/mol) and ^{t}Bu-urethane (Fig. S2 in Supporting information, 1701.23 L/mol) are much lower than that of earlier studies [32,36]. To our surprise, the weak hindered urethane bonds (HUrBs) tend to be more stable at higher temperature. As shown in Fig. 1c, the peak area for urethane at $\delta = 1.36$ ppm increased, while that for ^{t}BuOH at $\delta = 1.17$ ppm decreased with the increase of temperature, indicating that the bonding constants increased at elevated temperature. Such phenomenon is rare in literature since most reactions for bond formation is exothermic ($\Delta H < 0$) and generally associated with the loss of translational, rotational, and conformational entropy ($\Delta S < 0$), thus the Gibb's free energy ΔG ($\Delta G = \Delta H - T\Delta S$) becomes less negative at elevated temperature and the binding constants would be decreasing ($\Delta G = -RT\ln K_{eq}$). We calculated the ΔH and ΔS of this reaction from the equilibrium constants (Fig. 1d) in different temperatures (Fig. S3 in Supporting information). It was found that ΔH is positive and very small (16.2 kJ/mol) as expected, while ΔS is positive (124.4 J mol^{-1} K^{-1}), which is uncommon for normal reactions. With a positive but small ΔH and positive ΔS, ΔG will decrease upon heating. As a result, the urethanes using *tert*–butyl as steric hinderance becomes more stable and stronger before degradation.

In order to investigate the kinetic properties of the HUrBs, a series of exchange reactions were deployed (Fig. 2a), and the time resolved ^{1}H NMR spectra at different temperatures were collected (Fig. 2b and Fig. S4 in Supporting information). The concentration of *n*-pentyl-urethane (^{n}P-urethane) and ^{t}Bu-urethane were proportional to the peaks' areas in the ^{1}H NMR spectra, and the concentration of ^{t}Bu-urethane was displayed in Fig. 2c (and Table S1). The reaction rate constant k_{-1} for ^{t}Bu-urethane dissociation was determined to be 0.105 h^{-1} at 80 °C (Fig. 2d) and 0.318 h^{-1} at 120 °C (Fig. S5 in Supporting information). The activation energy of dissociation was determined to be 31.95 kJ/mol through the Arrhenius equation by using the data of 80 °C (353 K) and 120 °C (393 K). Therefore, the HUrB is weak in thermodynamic and inert in kinetic at low temperature, but stable in thermodynamic and active in kinetic at relative high temperature. Such features are favorable constructing stable but dynamic polymers.

Polyurethane containing hindered urethane bonds (PHUrs) was then synthesized by poly-addition reaction of 2,5-dimethyl-2,5-hexanediol (DMHDO), hexamethylene diisocyanate (HDI) and poly(hexamethylene diisocyanate (PHDI) (Fig. 3a). The polyurethane without hinderance was also synthesized using butanediol (BDO) instead of DMHDO. The polyurethane was characterized by FT-IR, as shown in Fig. 3b. Compared with the spectra of HDI and DMHDO, it could be observed that the peak for -NCO groups at 2252 cm^{-1} was vanished after reaction, while the peak of –OH at 3262 cm^{-1} was shifted to 3331 cm^{-1}. The board peak at 3331 cm^{-1}, corresponding to the N–H stretching of urethane bonds, appeared in the spectrum of polyurethane. These results confirmed the successful synthesis of polyurethane.

There were vast differences between the polyurethanes of different PHDI ratio, the transparency increased as the PHDI ratio increased. When the PHDI ratio is high enough (higher than 20%), the transparency of the resulting polyurethane is higher than 85% in the range of visible light (400–800 nm) (Fig. S6 in Supporting information). What is more, polyurethane with over 40% PHDI showed tendency to shrink even at room temperature. So, the surfaces of samples with high ratio became rough after a short time (Fig. 3c). The thermal properties of polyurethane were measured by means of STA and DSC. As shown in the STA spectra (Fig. S7 in Supporting information), the decomposition temperature of PHUrs (219 °C) is lower than that of the control sample without hindered urethane (297 °C). However, it is still high enough for normal application. Meanwhile, the glass transition temperatures (T_g) were changed only in a small range from 26 °C to 45 °C (Fig. 3d). The solid-to-solid phase transition [44] and melting peaks at 124 °C and 158 °C for the control sample without steric hinderance (Fig. S8 in Supporting information) were shifted to 104 °C and 144 °C for the PHUrs, indicating that the steric hinderance of the structure of *t*–butyl can reduce the crystallization.

With the change of PHDI ratio, the mechanical properties of the resulting polymers change significantly. As shown in Fig. S9 (Supporting information), the polyurethanes became stronger with the increase of PHDI ratios. The flexural modulus increased from 545 MPa to 2345 MPa in the PHDI ratio range of 0%–50%, and the processing time were also increased at the same time. Meanwhile, the fracture strain changed only slightly in the range of 1.3%–4.0%. The flexural modulus and fracture strain of PHUr-30% reached 1833 ± 50 MPa and 3.1%, while the processing time was quite short (30 min). In consideration of transparency and mechanical properties, we focused on the characterization and analysis of PHUr-30% in the following experiments.

Classical CANs without catalyst can only be processed at a relative high temperature, because the covalent crosslink is hard to dissociate [45]. However, when it comes to HUrBs developed in this work, the polyurethane could be reprocessed and stay transparent at a very low temperature (60 °C) and pressure (100 kPa), due to the excellent dynamicity of the HUrBs (Fig. 4a). The tensile curves of PHUr-30% were shown in Fig. 4b. The polymer has a high tensile modulus of 1011 ± 29 MPa and elongation of ~4% with the breaking energy of 104.54 kJ/m^2 upon applying a flexural strength of 28.8 MPa. Meanwhile the three-point bending curves are presented in Fig. S10 (Supporting information), the flexural modulus was determined to be 1833 ± 50 MPa with a small elongation of ~3% before fracturing upon applying a flexural strength of 50.4 MPa, confirming the rigidity of the material. The samples' tensile modulus reached 963 ± 23 MPa after reprocessing under the same condition (95.3% of the original modulus) value. The flexural modulus still reached 1510 ± 24 MPa after being reprocessed for 15 times at 60 °C and 100 kPa, which is 82.4% of the original. What is more, the sample after being reprocessed for 15 times could still endure a load of 10 kg (Fig. 4c). These results showed that the PHUrs hold good reprocessability upon a moderate hot pressing.

The thermo-healing properties of PHUrs were illustrated in the method shown in Fig. 4d. The samples were modeled by hot pressing at 120 °C and cut to simulate the damages. As shown in Fig. 4e, the damages on polyurethane could be healed quickly at relative low temperatures. The damages disappeared completely in 5 min at 50 °C, while it cost another 5 min at 40 °C. At 30 °C, the dam-

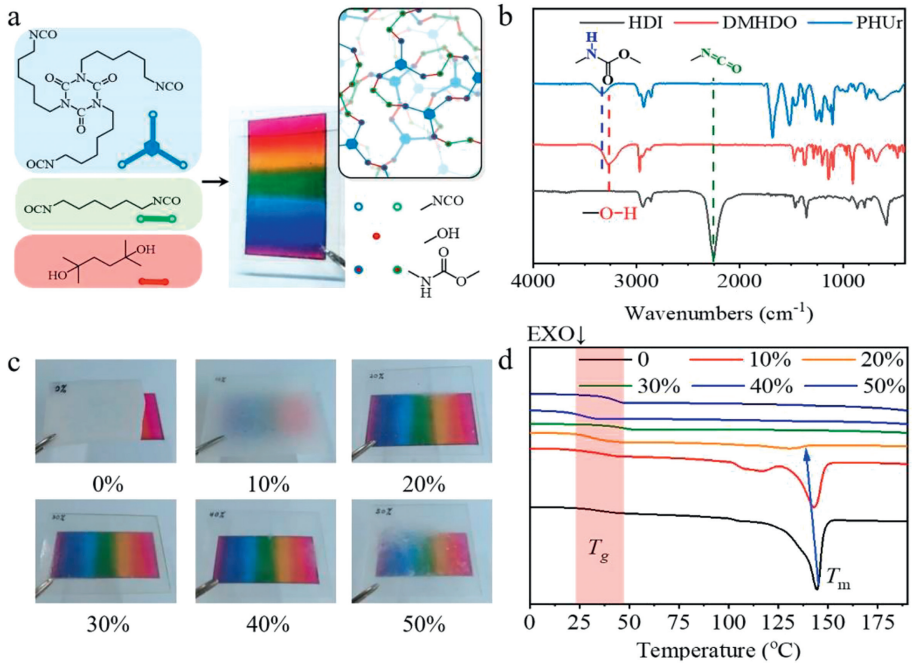

Fig. 3. (a) Synthesis of PHUrs. (b) The FT-IR spectra of HDI, DMHDO and PHUr. (c) Images of PHUrs with different PHDI ratio (from 0% to 50%). (d) DSC spectra of PHUrs with different PHDI ratio.

ages could not be healed well, the wound was still visible after 10 min, suggesting that more time is needed to eliminate it. These results showed the good abilities of HUrBs in healing, which enable the polyurethane healing at low temperatures under pressure of 100 kPa.

The creep and stress relaxation tests can show more details of polyurethane in rheology. The results of creep tests were shown in Fig. S11 (Supporting information). It showed good creep resistance with maximum creep strain of 2.0% in 20 min. What is more, our PHUrs showed great differences from normal CANs in stress relaxation. As shown in Fig. 4f, the relaxation time was increased at higher temperature, while the residual stress was also higher. This phenomenon indicated that there is higher creep resistance in the polyurethane's structure at higher temperature. From what we

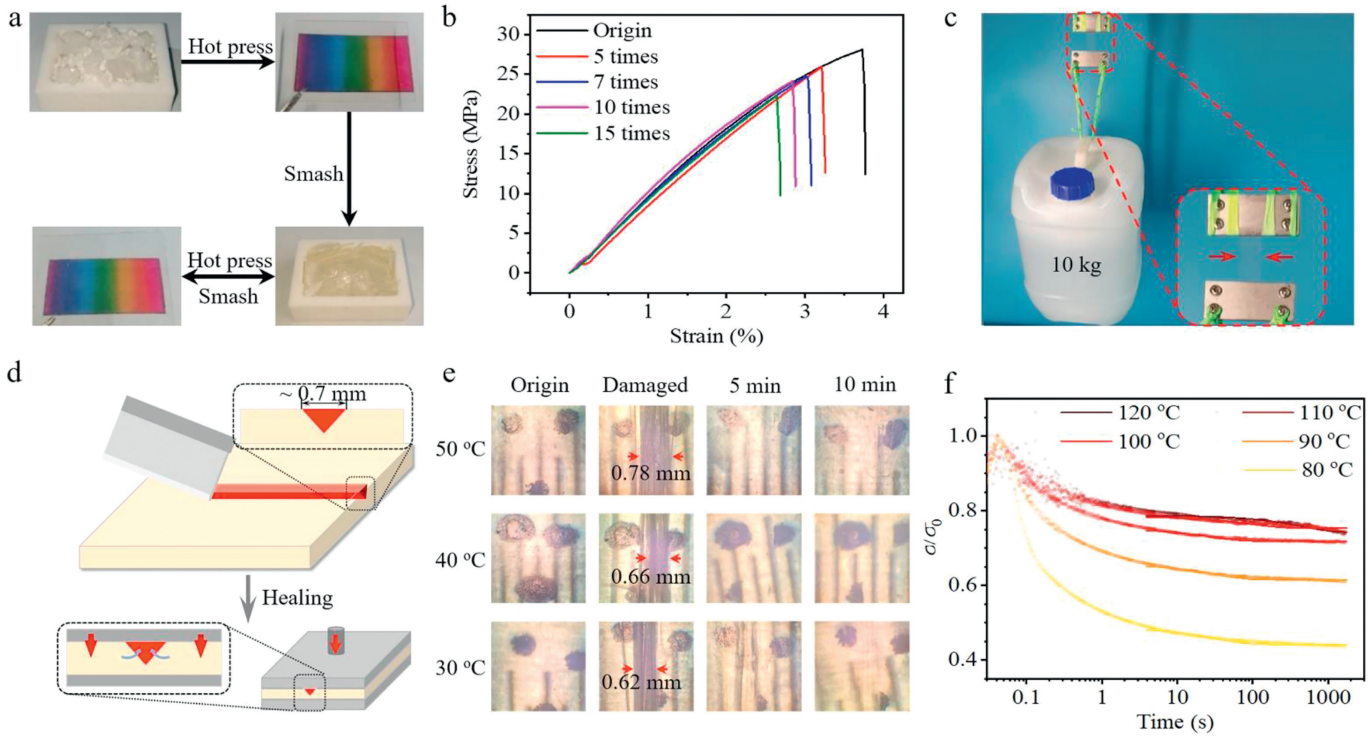

Fig. 4. (a) Processing and reprocessing of PHUrs through compression molding at 60 °C and 100 kPa for 30 min. (b) Tensile stress-strain curves of polyurethane after reprocessing at 60 °C. (c) The polyurethane after times of reprocessing can still withstand a full force of 10 kg. (d) The schematic diagram of damage simulation on PHUrs. (e) The photographs before and after healing under 100 kPa at different temperatures. (f) Stress relaxation curves of polyurethane at different temperatures.

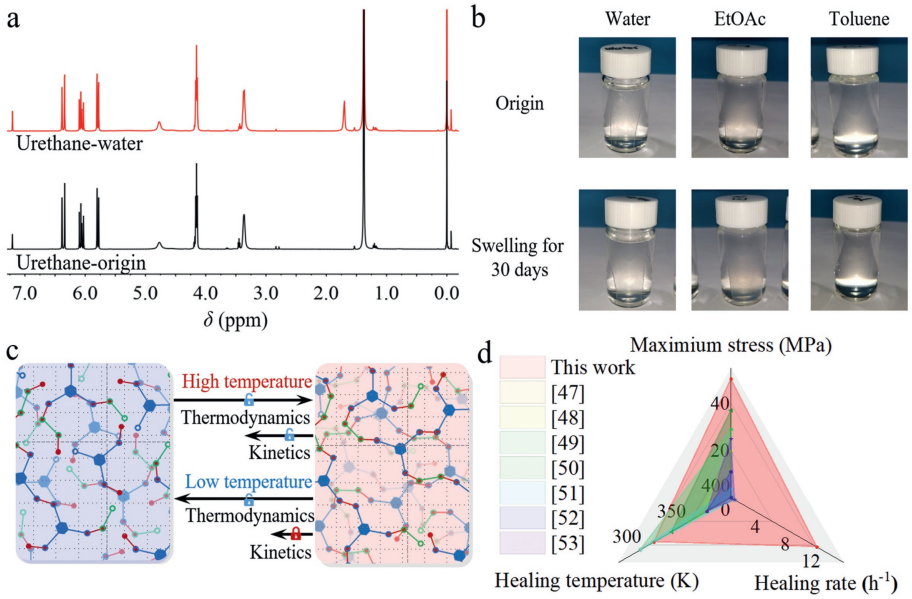

Fig. 5. (a) The ^{1}H NMR spectra of ^{t}Bu-urethane before and after treating with water for 24 h. (b) The photographs of polyurethane samples swelled in water, EtOAc and toluene, and after swelling for 30 days. (c) The relationship between thermodynamics and kinetics of PHUrs. (d) Comparison of mechanical and healing properties of reported materials [47–53] and this work.

have discussed above, the equilibrium constant of HUrBs increased as temperature became high. So, the crosslinking ratio and molecular weight were higher upon heating and thus gave higher creep resistance, which could stabilize the polyurethane and reduce the relaxation and creep.

Water and alcohol can cause irreversible damages to traditional dynamic urea bonds, limiting the practical applications of CANs based on hindered urea bonds [32]. We then studied the stabilities in solvents of dynamic urethane bonds. The FT-IR spectra of dynamic urethane before and after treating in water were obtained and displayed in Fig. S12 (Supporting information). The ^{1}H NMR spectra before and after treating in solvents containing water or ethanol were shown as Fig. 5a and Fig. S13 (Supporting information). There was no new signal attributed to the dissociated products in the spectra, which indicated that the hindered urethane bond dissociated extremely slow or nearly not dissociated at relative low temperature. Therefore, the HUrBs were stable in solvent due to the low rate constant in kinetics at relative low temperatures.

Moreover, the swelling rates of polyurethane in common solvent were obtained from curves in Fig. S14 (Supporting information). The PHUr-30% has good stability in water, the maximum water swelling capacity only reached 2.48% in 720 h, and there seems no obvious change of the sample bar (Fig. 5b). Meanwhile, the polyurethane was easy to be tumefied in organic solvent like ester and toluene. The polyurethane samples were tumefied very quickly in the first 24 h then continued to swell slowly, resulting in the increasement of total mass.

The excellent dynamic property and solvent stability can be illustrated by the unique thermodynamic and kinetic properties of the HUrBs (Fig. 5c). The K_{eq} and k_{-1} of polyurethane are increased upon heating, leading to rapid bonds exchanging. As a result, reprocessing and healing can be proceeded without affecting the stability of materials. On the opposite, the K_{eq} and k_{-1} are low at relative low temperature. When the polyurethane is cooled, the reactions of both formation and dissociation are freezed. A material with high molecular weight and high crosslinking density can be obtained. Meanwhile, the material is in non-equilibrium state, but the low k_{-1} lock the dissociation reaction and stabilizes the material. The timescale for bonds exchanging rate was decreased significantly at ambient and near-ambient conditions, thus high mechanical properties of PU was maintained [46]. As a result, compared to reported self-healing polyurethane materials [47–53], PHUrs have comparable or even higher mechanical properties while can be quickly healed and reprocessed at lower temperature (Fig. 5d) [54].

In summary, the *tert*–butyl group was introduced into the urethane bonds as hindrance, endowing them with dynamic property. Different from traditional dynamic bonds, the bonding constant of hindered urethane bonds were small at relative low temperature but could still stay stable due to the inert kinetic. With the positive but small ΔH (16.2 kJ/mol) and positive ΔS (124.4 J mol^{-1} K^{-1}) of the polymerization reaction, the bonding constant of ^{t}Bu-urethane rose from 526 L/mol (at 20 °C) to over 10^{4} L/mol (at 60 °C). Moreover, the active energy was a quite high (31.95 kJ/mol), thus the kinetic constant of counter reaction was low at room temperature for normal use. The polyurethane based on it showed good properties in both mechanical and reversibility. The Youngs' modulus of material reached 1011 ± 29 MPa and flexible modulus reached 1833 ± 50 MPa, while the polyurethane could be reprocessed at 60 °C under 100 kPa in 30 min. Even the equilibrium was not favoring for the formation of polymer at room temperature, the extremely low speed of counter reaction stabilized the polyurethane by stopping the counter reaction. Moreover, because of the low speed of dissociation, the material showed good stability in water and alcohol, which is always a fatal disadvantage of HUBs [55].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109305.

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