

# Oxime-Based and Catalyst-Free Dynamic Covalent Polyurethanes

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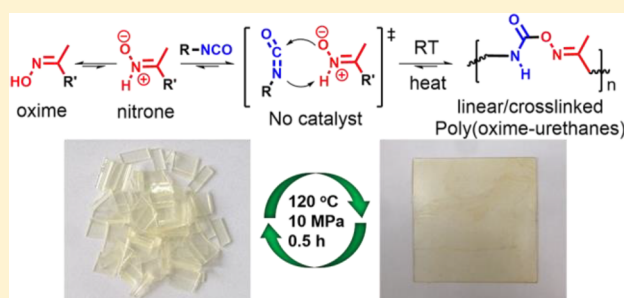
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## Supporting Information

**ABSTRACT:** Polyurethanes (PUs) have many applications resulting from their preeminent properties, but being commonly used toxic catalysts, and the lack of processability for PU thermosets cause limitations. Herein, we report a new class of the PU-like dynamic covalent polymers, poly(oxime-urethanes) (POUs), which are prepared from the uncatalyzed polyaddition of multifunctional oximes and hexamethylene diisocyanate (HDI) at ambient temperature. Kinetics studies reveal that almost complete polymerization (~99% conversion) can be achieved in 3 h at 30 °C in dichloromethane (DCM), the most effective among the solvents evaluated, producing linear POUs with comparable molecular weights to the catalyzed PUs. We find that the oxime-carbamate structures are reversible at about 100 °C through oxime-enabled transcarbamoylation via a thermally dissociative mechanism. The cross-linked POUs based on oxime-carbamate bonds show efficient catalyst-free healable/recyclable properties. Density functional theory (DFT) calculations suggest that the fast oxime-urethanation and the mild thermoreversible nature are mediated by the characteristic nitron tautomer of the oxime. Given widespread urethane-containing materials, POUs are of promising potential in applications because of the excellent mechanical performances, facile preparation, and dynamic property without using catalysts.

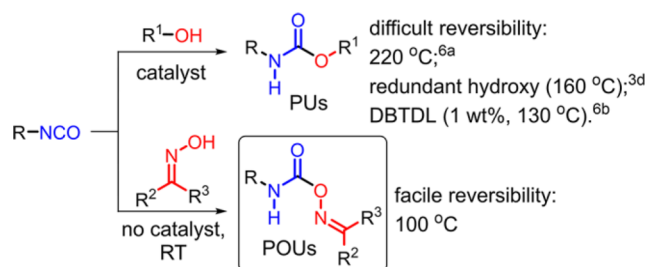


## INTRODUCTION

Covalently cross-linked polymers with excellent creep or environmental resistance, mechanical strength, and thermal stability possess significant applications in many fields.<sup>1</sup> As a result of their permanent structures, thermosets generally cannot be reshaped, reprocessed, or recycled. The fabrication of polymer networks with high performance and recyclability by a facile method is a great challenge. To achieve plasticity in cross-linked polymers, a great deal of effort has been devoted to introducing dynamic covalent bonds<sup>2</sup> into the networks, such as Diels–Alder cycloaddition, transesterification, transalkylation, transcarbamoylation, olefin metathesis, reversible radical chemistry, imine linkage, siloxane equilibration, and so on.<sup>3</sup> PUs, generally synthesized from polyisocyanates and polyols, are a very versatile group of materials in domestic and industrial applications.<sup>4</sup> Catalysts like highly toxic organotin compounds are commonly used in the manufacturing of PUs, especially for aliphatic isocyanates, albeit they are tough to remove from PUs.<sup>4b,5</sup> In addition, the extremely strong carbamate linkages endow covalently cross-linked PUs with high performance; however, this leads to intractable problems of recycling and reprocessing.<sup>6</sup> Therefore, repairable PU thermosets always demand the implantation of additional dynamic bonds or redundant nucleophilic hydroxy groups (Scheme 1).<sup>3d,i,7</sup> It is

quite desirable to develop a simple strategy for both effective urethanation and plasticity in the absence of catalysts.

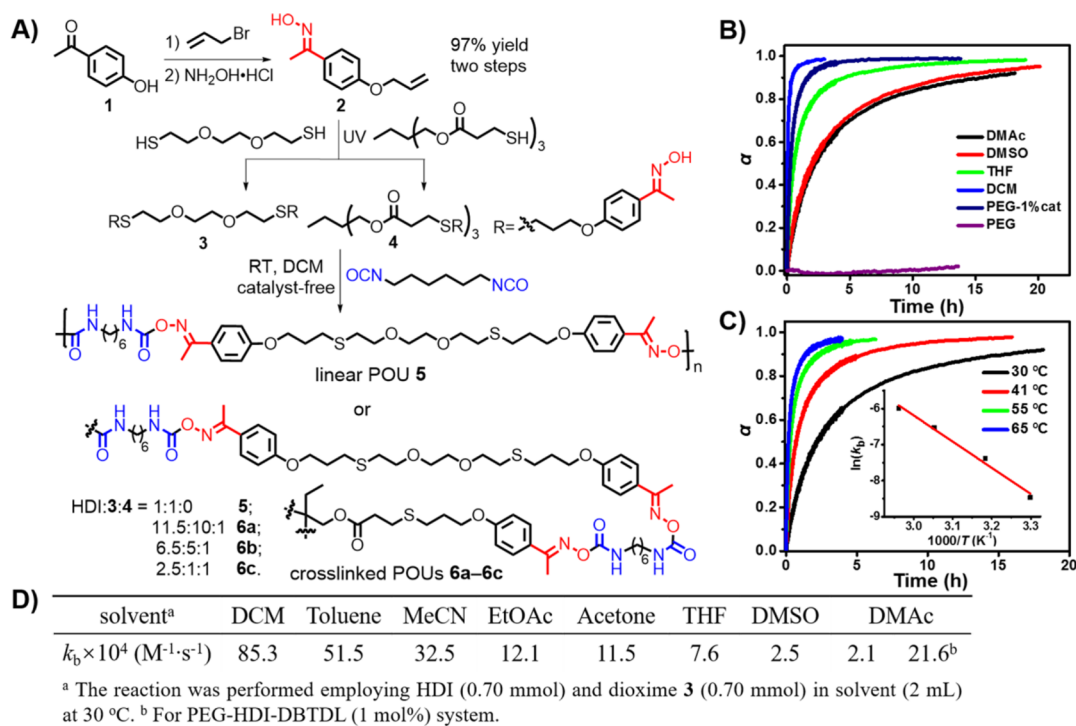
### Scheme 1. Preparation and Dynamic Nature of Traditional PUs (DBTDL = Dibutyltin Dilaurate) and POUs



Oximes, usually generated by the condensation of hydroxylamine and aldehydes or ketones with a high reaction efficiency, are particularly promising in the synthesis of multifunctional materials.<sup>8</sup> As a member of imine family, oximes show certain reversibility; however, the superior stability of oxime bonds causes a limitation in constructing dynamic covalent bulk

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**Figure 1.** (A) Synthesis of multifunctional oximes and linear/cross-linked POU. (B) Isocyanate conversion ( $\alpha$ ) as a function of time for the polyaddition reaction of dioxime **3** with HDI in different solvents at 30 °C. Polyethylene glycol (PEG,  $M_n = 400$ )-HDI systems with/without the catalyst of DBTDL were conducted in DMC for comparison. (C) Isocyanate conversion as a function of time at different temperatures in DMC (the inset shows the Arrhenius plot). (D) The second-order rate constants in various aprotic solvents at 30 °C (Figure S2).

materials.<sup>9</sup> Oximes have been utilized as blocking molecules for isocyanates, which can be removed at a relatively moderate temperature ( $\sim 100$  °C).<sup>10</sup> Despite being discovered in the 1880s<sup>10f</sup> and the great potential of oxime-carbamate bonds as a type of dynamic covalent bond in various systems, the kinetic and thermodynamic characteristics of oxime-carbamate bonds have not been intensively investigated until now,<sup>10d,e</sup> and their dynamic nature is yet to be explored. On the basis of dynamic oxime-carbamate bonds, herein we report an ambient-temperature, catalyst-free preparation of poly(oxime-urethanes) as a new type of thermally reversible covalent polymers from polyoximes and HDI. According to our experiments and DFT calculations, it is proposed that the isomeric nitron plays a key role in the processes of oxime-promoted fast urethanation and transcarbamoylation reaction, which is distinctive from traditional carbamates.

## RESULTS AND DISCUSSION

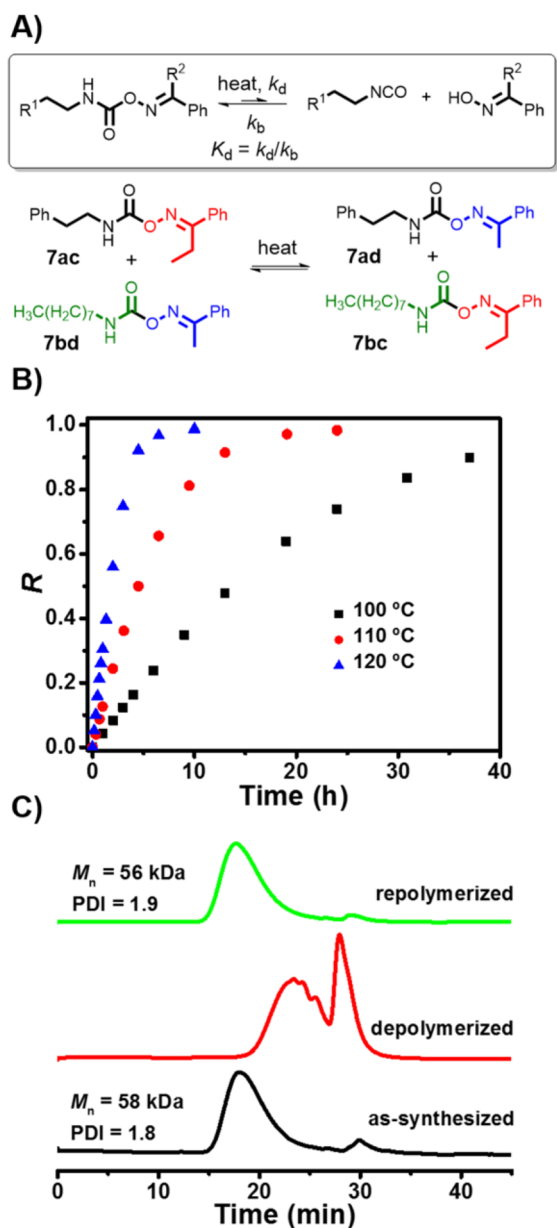
### Polymerization and Kinetics Studies of Linear POU.

To incorporate better stability<sup>8b,10f,11</sup> and strength into POU, dioxime **3**, with acetophenone moieties and a flexible link, was designed as the monomer and handily prepared from piceol (**1**) through thiol-ene reaction<sup>12</sup> in three steps (Figure 1A). Then, the kinetics of the solution polymerization between HDI and dioxime **3** (HDI/3 = 1:1) were studied by in situ Fourier transform infrared spectroscopy (FTIR) in various aprotic solvents (Figures 1B and S2). The formation of oxime-carbamate bonds was confirmed by the disappearance of asymmetric stretching of the NCO group at  $2276\text{ cm}^{-1}$ , the enhanced carbamate N-H bending vibration at  $1500\text{ cm}^{-1}$  and a new strong peak in the carbonyl absorption at  $1735\text{ cm}^{-1}$  which corresponded to oxime-linked carbamates. Like the uncatalyzed alcoholysis reaction of isocyanate,<sup>4c,13</sup> the oxime-

urethanation is first-order for HDI and for dioxime **3** (Figure S1), with the highest reaction conversion of 99% after 3 h and the largest second-order bonding rate constant  $k_b$  of  $8.5 \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$  in DCM at 30 °C (rate =  $k_b[\text{oxime}][\text{NCO}]$ ). This prominently outperformed the DBTDL-catalyzed (1 mol %) PEG-HDI system for common PUs. Moreover, the magnitude of the reaction rate constants varies 40-fold in the order of DCM > toluene > MeCN > EtOAc  $\approx$  acetone > tetrahydrofuran (THF) > dimethyl sulfoxide (DMSO)  $\approx$  *N,N*-dimethylacetamide (DMAc) (Figure 1D). This series is closely related to the empirical hydrogen-bond strength between the solvent acceptor and the oxime donor.<sup>14</sup> In striking contrast, isocyanate-alcohol systems show the highest reactivity in DMAc and DMSO.<sup>13c</sup> Considering the stronger hydrogen-bonding capabilities of oximes than the corresponding alcohols,<sup>14b,15</sup> the rate-retarding effect in oxygen-containing solvents should be attributed to the stronger ability of the solvent acceptor to associate with oxime, thereby decreasing the availability of the oxime groups to react with isocyanate. The slowest reaction rate in DMAc, with an Arrhenius activation energy  $E_{a,b}$  of about  $14.4\text{ kcal}\cdot\text{mol}^{-1}$  (Figure 1C), is still approximately 45-fold faster (90% conversion after 14 h) than that of the usual PEG-HDI system, which just showed  $\sim 2\%$  conversion without a catalyst (Figure 1B). More importantly, POU **5** achieves a number-average molecular weight ( $M_n$ ) up to  $\sim 60\text{ kDa}$ , which is comparable to the catalyzed PUs<sup>5b</sup> (Figure S3). We believe that this highly efficient, metal-free polyaddition of oximes to isocyanates would benefit the preparation of many polyurethane materials and have enormous advantages in environmentally benign applications.<sup>4b,5b</sup>

**Thermal Reversibility in Model Compounds and Linear POU.** We employed variable-temperature NMR to

directly observe the thermal dissociation of oxime-carbamate **7bd** to octyl isocyanate and acetophenone oxime. An 11% conversion with an equilibrium constant  $K_d$  of  $3.2 \times 10^{-3}$  M at  $120^\circ\text{C}$  was observed (Figure S4). The small equilibrium constant suggests that the sluggish net bond dissociation would be insufficient for reprocessing at such temperatures ( $\sim 120^\circ\text{C}$ ) through a bond breaking/reforming procedure such as the reversible Diels–Alder reaction ( $K_d \approx 1.7$  M,  $120^\circ\text{C}$ ).<sup>16</sup> Additionally, to further examine the utility of reversible oxime-carbamate bonds, two model compounds (**7ac** and **7bd**) were used to study the transcarbamoylation reaction by liquid chromatography–mass spectrometry (LC–MS) (Figure 2A). When the mixture was heated, two new oxime-carbamates **7ad** and **7bc** were formed (Figure S6). By following the area ratio  $R$



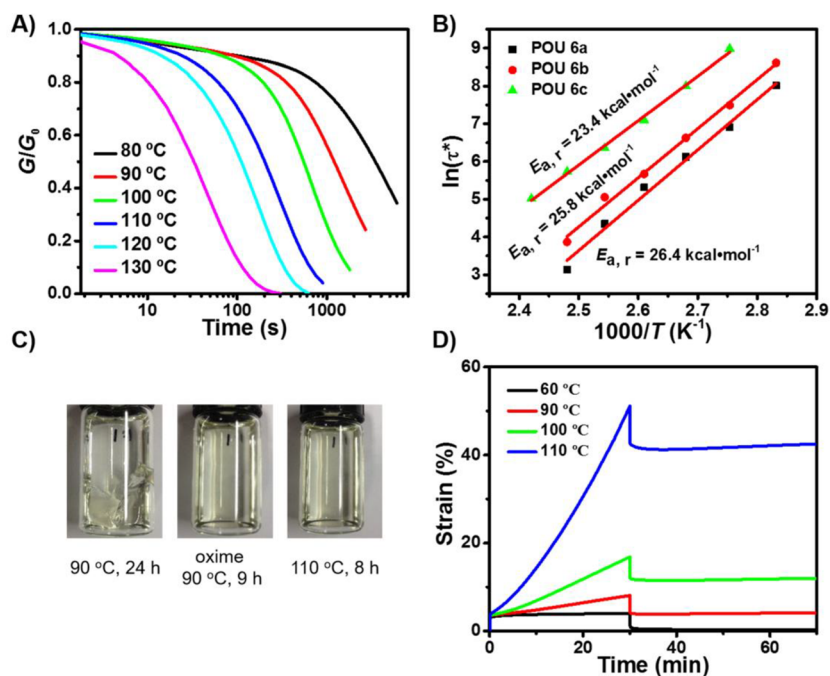
**Figure 2.** (A) Oxime-enabled transcarbamoylation reaction via a dissociative approach. (B) Chromatographic peak area ratio  $R$  as a function of time upon heating the mixture of **7ac** and **7bd** at different temperatures. (C) GPC analysis of the dynamic depolymerization and repolymerization of POU 5 in *N,N*-dimethylformamide.

$= (7ad + 7bc)/(7ac + 7bd)$  with time, we found that the temperature profoundly influences the transcarbamoylation reaction rate. Thermodynamic equilibrium was reached in 6 h at  $120^\circ\text{C}$  (Figure 2B). Arrhenius analysis of the model reaction gave a transcarbamoylation activation energy ( $E_{a,t}$ ) of  $28.2$  kcal·mol<sup>-1</sup> (Figure S6), which is significantly lower than those for residual hydroxyl-assisted<sup>3d</sup> or catalyzed transcarbamoylations<sup>6b</sup> of general alcohol systems. Meanwhile, the large apparent dissociation rate constants ( $k_d = 0.09$  h<sup>-1</sup>,  $100^\circ\text{C}$ , Figure S7) provide the possibility that reversible oxime-carbamate bonds could be practicable in bulk polymers through a dissociative transcarbamoylation mechanism.<sup>17</sup> To preliminarily test our hypothesis about the dynamic behavior in polymers, the as-synthesized POU 5 was treated with 1 equiv of **3** at  $110^\circ\text{C}$  for 1 h. Remarkable degradation of POU 5 could be confirmed by the GPC curve; however, after the addition of 1 equiv of HDI to the reaction solution at  $60^\circ\text{C}$  for 5 h, the unimodal GPC curve which overlaid almost entirely with the original one was detected (Figure 2C). These preceding studies indicate that dynamic oxime-carbamate bonds exchange spontaneously at high temperature and are highly valuable in constructing dynamic polymers.

### Synthesis and Characterization of Cross-linked POUs.

HDI, dioxime **3**, and trioxime **4**, all with different ratios, were used to fabricate various cross-linked POUs in DCM at room temperature. This was followed by solvent removal at  $60^\circ\text{C}$  under vacuum. Similarly, the complete consumption of isocyanate and incorporation of oxime components were confirmed by attenuated total reflectance (ATR)-FTIR for all of the three cross-linked networks (Figure S9). Swelling experiments in THF ( $25^\circ\text{C}$ , 72 h) showed that the cross-linked POUs were insoluble, and the gel fractions of the densely cross-linked **6b** and **6c** are  $\geq 97\%$  (Table S2). The bulk POUs exhibit mechanical properties that are characteristic of elastomeric polymers, varying with different formulas. POU **6b** shows a breaking strain ( $\epsilon_b$ ) of  $677 \pm 11\%$  and a breaking stress ( $\sigma_b$ ) of  $49.1 \pm 2.2$  MPa; these are comparable with commercial PU thermosets (Table S3).<sup>3d,4a,7a</sup> Dynamic mechanical analysis (DMA) shows POUs having two abrupt drops in their storage modulus, arising from the immiscibility of the soft poly(thio)ether and the hard aryl oxime-carbamate blocks (Figure S10).<sup>7a,18</sup> The microphase-separated structure was also detected by atomic-force microscope (AFM) morphology analysis (Figure S11). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) investigations gave a glass-transition temperature ( $T_g$ ) of  $30^\circ\text{C}$  and a good thermal stability with a weight loss of 5% at  $235^\circ\text{C}$  for POU **6b** (Figures S12 and S13). As the result of an increase in the equivalents of the utilized cross-linker, the estimated molecular weights between cross-links ( $M_c$ ) decrease from 5.6 to  $1.9$  kg·mol<sup>-1</sup> (Table S2), which is accompanied by a high modulus and a low deformability (Table S3). All of these phenomena demonstrate that oxime-based urethanation can be completed with practical preparation protocols resulting in high-performance urethane-containing materials.

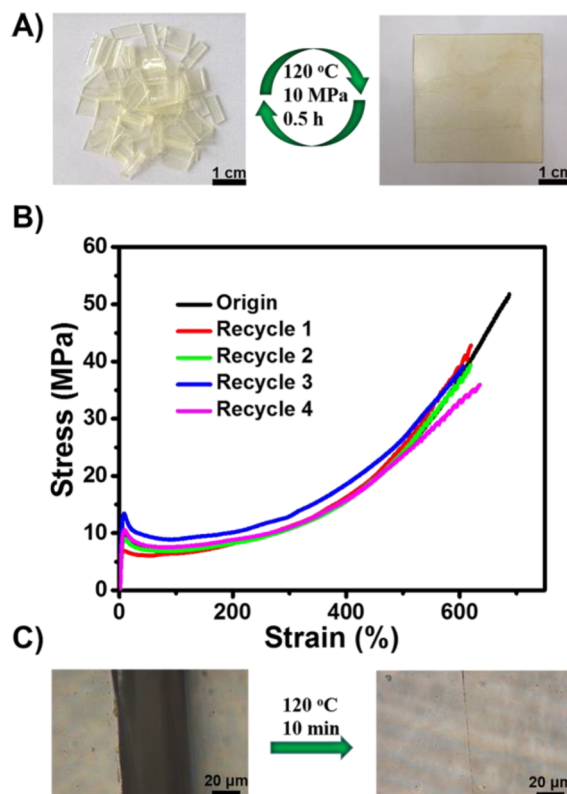
**Thermal Reversibility in Cross-linked POUs.** We investigated the plasticity of the cross-linked POUs by conducting time- and temperature-dependent stress-relaxation analysis (Figures 3A and S14). As expected, the modulus decreases faster along with an increase in temperature or a decrease in cross-linking density. However, Arrhenius analyses of these POUs obtain comparable relaxation activation energies (Figure 3B), which are in close agreement to the trans-



**Figure 3.** (A) Normalized stress-relaxation analysis of POU **6b**. (B) Determination of relaxation activation energy ( $E_{a,r}$ ) from Arrhenius analysis of the characteristic relaxation time  $\tau^*$  versus  $1000/T$  for cross-linked POUs. (C) The solubility of POU **6c** in DMAc: swollen (left, 90 °C, 24 h), dissolved (middle, 90 °C, 9 h, with an excess of acetophenone oxime), and dissolved (right, 110 °C, 8 h, without the oxime). (D) Tensile creep-recovery behaviors of POU **6b** with an applied stress of 0.1 MPa at elevated temperatures.

carbamoylation activation energy in model compounds **7**. These results have been interpreted as evidence that transcarbamoylation dominates the relaxation behavior in POU thermosets. As for these systems, the topology freezing-transition temperatures<sup>3b</sup> ( $T_v$ , where the viscosity reaches  $10^{12}$  Pa·s) are 31–48 °C, slightly higher than their  $T_g$ , which means the cross-linked POUs are viscoelastic liquids in the major range of the rubbery state (Table S2). The well-fitted Angell fragility plots<sup>19</sup> show that upon heating, the viscosity gradually decreases in accordance with the Arrhenius law, just like typical silica glass and other vitrimers<sup>3b,p</sup> (Figure S15). Such transcarbamoylation is accomplished through a dissociative intermediate, which is different from the well-known associative vitrimers. The complete dissolution of **6c** in DMAc either alone at 110 °C or at 90 °C with an excess of the oxime group coincides with the aforementioned relaxation mechanism via dissociative transcarbamoylation<sup>3i</sup> (Figure 3C). Consistent with stress relaxation experiments, the creep-recovery experiments of **6b** confirmed that it behaves as a permanently cross-linked elastomer when transcarbamoylation is frozen (60 °C). However, at high temperatures (>90 °C), after the elastic response, an evident deformation increase ( $\sim 1.6\%$  min<sup>-1</sup>, 110 °C) and high residual strain (40%, 110 °C) are perceived, as topology rearrangements are activated (Figures 3D and S16). Therefore, the fluidity of vitrimer-like<sup>3p</sup> POUs is controlled by thermally stimulated dissociative transcarbamoylation.

To further investigate the recyclability, the POU networks were cut into small pieces and then hot-pressed to reform the bulk materials (Figure 4A). Static tensile tests proved that POUs were able to recover most of their mechanical properties even after multiple cycles (Table S3, Figures 4B and S17). Typically, the first-recycled POU **6b** has the maximum recovery upon hot-pressing for  $\sim 30$  min (Figure S18), with an 82% recovery in  $\sigma_b$  and a 90% recovery in  $\epsilon_b$ , both of which are more effective than the residual hydroxyl-assisted system.<sup>3d</sup> In



**Figure 4.** (A) Recycling of POU **6b** pieces (left) by compression molding to reform the bulk material (right, the 4th cycle). (B) Stress-strain curves of the original and the recycled **6b**. (C) Microscopic images of two pieces of **6b** film before (left) and after (right) thermal self-healing.

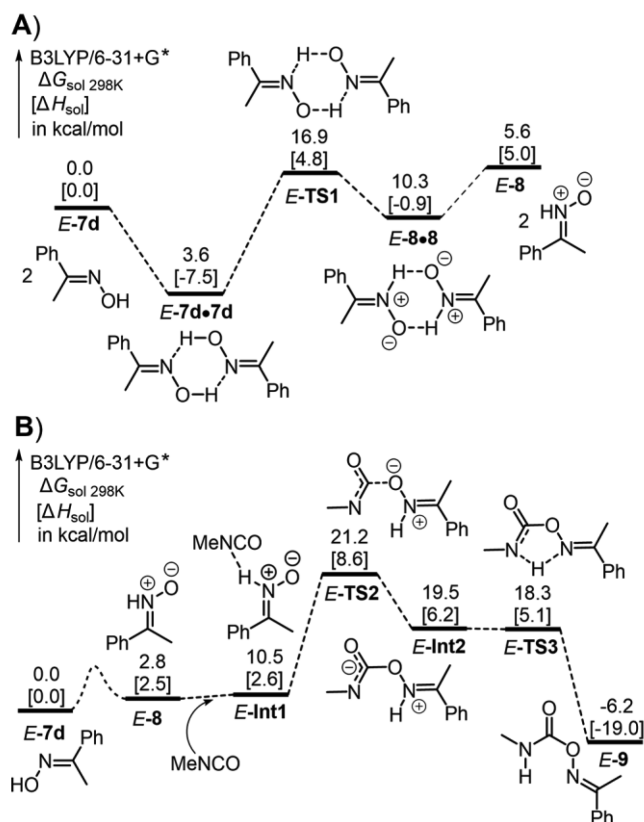
conjunction with the model transcarbamylation reaction (Figure S6), the absence of IR absorption by the NCO group, and the recovery of the plateau modulus for the recycled POUs illustrate that there is no substantial net dissociation of oxime-carbamates in polymers (Figures S19 and S20). In addition, a thermal self-healing experiment was also performed to evaluate the remendable ability free of pressure. After cutting the rectangle film of **6b** into two pieces with a razor blade and gently bringing the two pieces into contact for subsequent healing at 120 °C for 10 min without external force, it was found that the notch on the film almost disappeared and the healed sample could load up to ~5 kg (Figures 4C and S21). These efficient and fast-repairing performances can be ascribed to the dynamic oxime-promoted transcarbamylation.

## COMPUTATIONAL STUDIES

We would like to emphasize that, compared with previously reported polyurethanes or polyhydroxyurethanes,<sup>3d</sup> the POUs integrate with two notable characteristics. The polymerization of oximes and isocyanates can not only be completed without catalysts under ambient temperature, but the elegant oxime structure in carbamate could also dramatically facilitate the transcarbamylation reaction through a dissociative approach. These unique features interested us, so we examined the mechanisms of the oxime-based urethane formation and exchange reaction, with the aid of DFT calculations<sup>20</sup> (B3LYP method using 6-31+G\*) using *E*-acetophenone oxime (*E*-7d) and methyl isocyanate (MeNCO) as model substrates (see the Supporting Information).

**Urethanation Mechanism.** Theoretical studies disclosed that the direct concerted addition of an oxime to isocyanate via a four-membered ring transition state (similar to an alcoholysis reaction<sup>21</sup>) requires an activation enthalpy as high as 32.7 kcal·mol<sup>-1</sup> (Scheme S13), suggesting that such a process is not favored kinetically (the polymerization was conducted at room temperature). In addition, it is also possible that two or three oximes can react concertedly with isocyanate to give the adduct via six-membered or eight-membered ring autocatalytic transition states,<sup>22</sup> which require activation enthalpies of 23.4 or 22.0 kcal·mol<sup>-1</sup>, respectively (Figures S22 and S23). Considering that these multicomponent reaction pathways are disfavored entropically, such alternatives can be ruled out. These pathways involving more oximes do not fit the experimentally observed first-order kinetics for isocyanate and for oxime (Figures S1 and S2).

We found a novel and energetically favored pathway that can account for the experimental phenomena. It is known that an oxime can isomerize to its nitron tautomer,<sup>8b,23</sup> and our DFT calculations indicated that this isomerization is a bimolecular mechanism between two oximes via intramolecular proton-transfer processes.<sup>24</sup> The isomerization starts from forming a complex between two oximes (exothermic by 7.5 kcal·mol<sup>-1</sup>), which then undergoes proton transfer via *E*-TS1 with an activation enthalpy of 12.3 kcal·mol<sup>-1</sup>. The isomerization gives a complex of two nitrones, which can smoothly dissociate into two individual nitrones (Figure 5A). Once the nitron is generated, the urethanation begins with nucleophilic addition of the nitron to isocyanate from the nitron-isocyanate complex *E*-Int1, with an activation enthalpy of 6.0 kcal·mol<sup>-1</sup> (Figure 5B). This easy step (endothermic by 3.6 kcal·mol<sup>-1</sup>) is understandable because of the high nucleophilicity of nitron's oxygen, which bears a formal negative charge. The following step is an intramolecular hydrogen transfer via *E*-TS3 to give



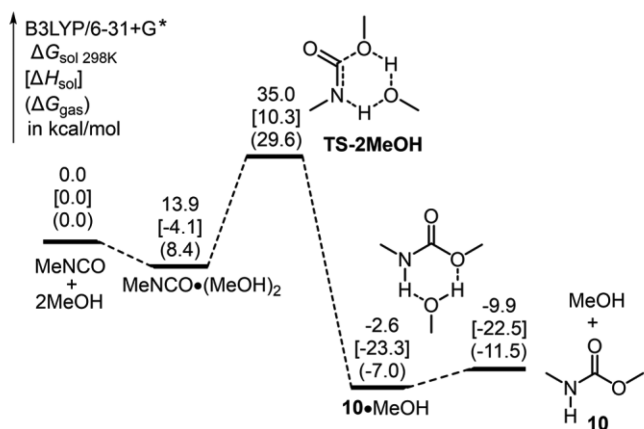
**Figure 5.** DFT-calculated energy surface for (A) bimolecular tautomerism of *E*-7d to *E*-8; (B) the reaction between *E*-7d and MeNCO.

the final addition product. This step is barrierless (*E*-TS3 is higher than intermediate *E*-Int2 by 1.5 kcal·mol<sup>-1</sup> in terms of single point energy, but with a zero-point energy correction, it is lower than *E*-Int2 by 1.1 kcal·mol<sup>-1</sup>) and exothermic by 25.2 kcal·mol<sup>-1</sup>.

According to the above calculations, the oxime-urethanation reaction has a fast isomerization to the nitron as the rate-determining step of the overall reaction is the nucleophilic addition of the nitron to the isocyanate with an activation enthalpy of 9.7 kcal·mol<sup>-1</sup> and an activation free energy of 21.9 kcal·mol<sup>-1</sup> at the higher level of B3LYP/6-31+G\*\* (from *E*-7d and MeNCO to *E*-TS2; the M06-2X method gave similar results with those of B3LYP: see the Supporting Information). The activation enthalpy and the activation free energy are close to the experimentally measured activation parameters ( $\Delta H_b^\ddagger = 13.8$  kcal·mol<sup>-1</sup>,  $\Delta G_b^\ddagger = 22.6$  kcal·mol<sup>-1</sup>, Table S4).

When an alcohol is used as the reactant (Figure 6), this has to proceed with the entropically disfavored three-molecule process (two alcohols and isocyanate in the transition state) with an activation free energy of 35.0 kcal·mol<sup>-1</sup>. Thus, compared to the nitron with a strong negative nucleophilic oxygen atom and easy protonation, alcohol shows a significantly lower reactivity with isocyanate.

**Transcarbamylation Mechanism.** The oxime-enabled transcarbamylation can be understood from the backward reaction of *E*-9 to *E*-7d and MeNCO through intramolecular hydrogen shift/dissociation processes,<sup>10d</sup> which requires an activation enthalpy of about 27.6 kcal·mol<sup>-1</sup> (from *E*-9 to *E*-TS2, Figure 5B). As for transcarbamylation of an alcohol, it normally needs additional nucleophiles to promote hydrogen



**Figure 6.** DFT-computed energy surface for the autocatalytic alcoholysis reaction of two molecules of MeOH and MeNCO.

transfer, such as the reverse autocatalytic dissociation reaction ( $\Delta H^\ddagger = 33.6 \text{ kcal}\cdot\text{mol}^{-1}$  from  $10\cdot\text{MeOH}$ , Figure 6) and the hydroxyl-assisted associative transcarbamoylation<sup>3d</sup> ( $\Delta H^\ddagger = 36.5 \text{ kcal}\cdot\text{mol}^{-1}$ , Scheme S16). Both are inferior to oxime-enabled transcarbamoylation. This difference can be ascribed to the presence of the oxime's nitrogen atom assisting intramolecular hydrogen transfer, and the weakening of C(O)–O bond in *E*-TS2 (1.957 Å, Figure S28; but for TS-2MeOH it is 1.541 Å, Figure S33).

## CONCLUSIONS

In summary, we synthesized dynamic poly(oxime-urethanes) from HDI and polyoximes in the absence of catalysts at room temperature. The obtained POUs possess mechanical properties competitive to traditional polyurethanes and outstanding repairable performance for cross-linked networks. The facile and effective relaxation behavior can be attributed to the oxime-promoted transcarbamoylation reaction. Kinetics experiments and DFT calculations have indicated that, in comparison with alcohol, the oxime is more reactive in the urethanation reaction and also improves the dynamic nature of traditional carbamates. This is because of the oxime's bifunctionality as the nucleophile (oxygen atom of nitron) and the proton acceptor (nitrogen atom). Furthermore, the easily accessible oximes<sup>8b</sup> and versatile isocyanates<sup>4a</sup> make it achievable to apply oxime–carbamate bonds into the design of catalyst-free, dynamic, and variable urethane-containing systems, which would be expected to expand the scope of dynamic covalent bonds<sup>2</sup> and conventionally widely used PUs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b03967.

Detail experimental procedures, characterization data, full citation of Gaussian 09 and details on kinetics, DFT studies(PDF)

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## Notes

The authors declare no competing financial interest.

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