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Boronic Ester Based Vitrimers with Enhanced Stability via Internal Boron−Nitrogen Coordination

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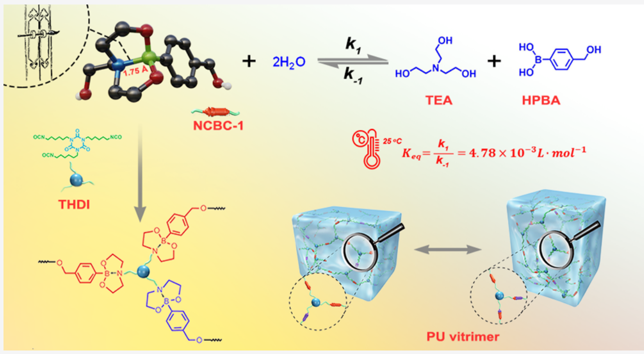

ABSTRACT: Boron-containing polymers have many applications resulting from their prominent properties. Organoboron species with reversible B−O bonds have been successfully employed for the fabrication of various self-healing/healable and reprocessable polymers. However, the application of the polymers containing boronic ester or boroxine linkages is limited because of their instability to water. Herein, we report the hydrolytic stability and dynamic covalent chemistry of the nitrogen-coordinating cyclic boronic diester (NCB) linkages, and a new class of vitrimers based on NCB linkages is developed through the chemical reactions of reactive hydrogen with isocyanate. Thermodynamic and kinetic studies demonstrated that NCB linkages exhibit enhanced water and heat resistance, whereas the exchange reactions between NCB linkages can take place upon heating without any catalyst. The model compounds of NCBC-X1 and NCBC-X2 containing a urethane group and urea group, respectively, also showed higher hydrolytic stability compared to that of conventional boronic esters. Polyurethane vitrimers and poly(urea-urethane) vitrimers based on NCB linkages exhibited excellent solvent resistance and mechanical properties like general thermosets, which can be repaired, reprocessed, and recycled via the transesterification of NCB linkages upon heating. Especially, vitrimers based on NCB linkages presented improved stability to water and heat compared to those through conventional boronic esters because of the existence of N → B internal coordination. We anticipate that this work will provide a new strategy for designing the next generation of sustainable materials.

INTRODUCTION

Thermosetting polymers, which are cross-linked by irreversible covalent bonds, are widely used for vast demanding applications because of their superior mechanical properties, dimensional stability, and chemical resistance. However, the cross-linked architecture limits the polymer chain's mobility, such that thermosets cannot be reshaped, reprocessed, or recycled once fully cured. Thus, thermosets are major contributors to environmental pollution and responsible for a significant waste of resources.[1] Introducing dynamic covalent bonds into polymer networks to prepare dynamic cross-linked polymers is an efficient way of providing reversible characteristics to traditional cross-linked polymers. Dynamic cross-linked polymers are able to change their topological structures via the exchange reactions of dynamic covalent bonds triggered by the external stimuli, while still retaining the mechanical properties of traditional cross-linked polymers. It not only brings malleability and recyclability to cross-linked polymers but also endows many excellent properties to traditional polymers, which has great scientific significance for promoting the development of sustainable materials.[2−4]

Generally, dynamic cross-linked polymers can be classified into two groups depending on their exchange mechanisms.[5] Leibler's group[6] defined dynamic cross-linked polymers based on associative exchange reactions like "vitrimers" because of their silica-like rheological behavior. Below the topology freezing temperature (T_v), vitrimers behave like traditional thermosets that exhibit excellent dimensional stability, chemical resistance, and mechanical properties. At higher temperatures, vitrimers can be repaired, reprocessed, and recycled via rapid exchange reactions of dynamic covalent bonds, while maintaining a relatively constant cross-linking density. In recent years, a variety of associative covalent exchange chemistries have been developed, such as transesterification, transalkylation, transcarbamoylation, siloxane equilibration, olefin metathesis, imine exchanges, and so on.[7−15]

Boronic ester linkages formed by boronic acids and diols are a typical class of dynamic covalent bonds;[16,17] their dynamic reversibility can be easily regulated by adjusting the pH value or ethanol concentration of the medium.[18−22] The unique

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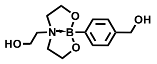
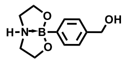
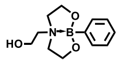
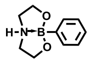
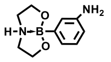
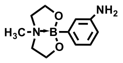
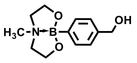
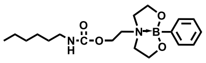
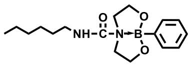
properties of boronic esters have been employed to create the porous covalent organic framework,[23] supramolecular polymers,[24,25] and self-healing materials.[26] Furthermore, boroxines formed by the dehydration of boronic acid can also be used to prepare dynamic covalent polymers.[27−30] Despite the fact that boronic ester and boroxine linkages have been successfully used in the preparation of various self-healing/healable materials, designing boronic ester based vitrimers with enhanced hydrolytic stability and superior mechanical properties remains extremely challenging, as both boronic esters and boroxines are very sensitive to water or alcohols.

Organoboron chemistry studies have established that the cyclic boronic diesters are more stable than the boronic acid monoesters, especially for the cyclic boronic esters coordinated by electron donors (e.g., nitrogen-donor compounds).[31] As mentioned above, we provide a new strategy for synthesizing stable nitrogen-coordinating cyclic boronic diester compounds (NCBCs) by introducing a N → B dative bond and then use them to construct a cross-linked network. Differing from most vitrimers, where dynamic covalent bonds were formed simultaneously with final materials, we first synthesized small-molecular model compounds containing dynamic covalent bonds, and the cross-linked networks were constructed on the basis of the dynamic linkages. This process is more conducive to the precise control of vitrimer structures. Although boronic esters with internal N → B interaction have been applied in cross-coupling reactions,[32] or employed as a curing agent for epoxy resin,[33] the thermodynamic and kinetic characteristics, as well as the dynamic nature of nitrogen-coordinating cyclic boronic diester (NCB) linkages, have not yet been systematically explored.

In this study, we first synthesized several NCBCs with different structures and studied their hydrolytic and exchange reactions, which demonstrated enhanced hydrolytic stability and rapid transesterification of NCB linkages. Furthermore, the model compounds of NCBC-X1 and NCBC-X2 were synthesized by reacting hexyl isocyanate with monofunctional NCBC-3 and NCBC-4 (Table 1), respectively, and their hydrolysis stability was studied. The hydrolysis stability of NCBC-X1 is comparable to that of NCBC, while NCBC-X2 is slightly inferior to NCBC. On the basis of the model compound results, polyurethane (PU) vitrimers and poly(urea-urethane) (PUU) vitrimers were prepared by reacting a trifunctional homopolymer of hexamethylene diisocyanate (THDI) with NCBC-1 and NCBC-2, respectively. PU vitrimers and PUU vitrimers not only inherit excellent properties of traditional thermosets but also can be repaired, reprocessed, and recycled through the exchange reactions of NCB linkages triggered by heating. The design concept is shown in Figure 1. To our knowledge, this is the first report on vitrimers with enhanced water resistance and excellent recyclability based on NCB linkages. We envision that this study will provide a more extensive option for vitrimer design, which is also an important means of achieving high-performance general purpose polymers.

Table 1. List of NCBCs

NCBCs	Chemical structures
NCBC-1	
NCBC-2	
NCBC-3	
NCBC-4	
NCBC-5	
NCBC-6	
NCBC-7	
NCBC-X1	
NCBC-X2	

RESULTS AND DISCUSSION

Synthesis of NCBCs and Evaluation of Their Hydrolytic Stability. For investigation of the hydrolytic stability and dynamic nature of the NCB linkages, seven model NCBCs were designed and synthesized (Schemes S1−S7 in the Supporting Information; Table 1). Conventional boronic esters synthesized from boronic acids with diols or phenols are very susceptible to water, so the water produced during the reaction must be continuously removed to ensure a complete reaction. When NCBCs are synthesized, a small amount of water does not matter because of the highly hydrophobic nature of the NCB linkages with the intramolecular coordination of N → B. The structures of NCBCs were confirmed by nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR), high-resolution mass spectrometry (HRMS), Fourier transform infrared (FTIR) spectra, and elemental analyses (Figures S1−S7 and Table S1). The melting points of NCBCs were shown in Figure S8. The strong coordination of N → B was confirmed by single-crystal X-ray diffraction. At room temperature, the boron−nitrogen bond length in NCBC-1 and NCBC-3 were ∼1.75 Å, while that for NCBC-2 and NCBC-4 was ∼1.66 Å, which was between the length of the boron−nitrogen covalent bond (e.g., in boron nitride, 1.53 Å) and the N → B external coordination bond (1.80−1.98 Å).[34] The results indicate that NCBCs show higher stability than the boronic esters with external coordination structures. Data of single-crystal X-ray diffraction are shown in Figures S9−S12 and Tables S2−S13.

The hydrolytic stability of NCBCs was investigated by taking NCBC-1 and NCBC-2 as examples. Specifically, we dissolved NCBC-1 in DMSO-d_6 with different water concentrations, and the hydrolysis stability of NCBC-1 was evaluated by ^{1}H NMR (Figure 2, Figure S13 and Table S14). NCBCs showed higher hydrolysis stability than those of conventional boronic esters because of the intramolecular coordination of N → B in the NCB linkages. For example, when water was added to NCBC-1 or NCBC-2 in a molar ratio of 20:1 (approximately 20 equiv compared to boronic ester groups), the hydrolysis percentages of NCBC-1 and NCBC-2 were 15.8% and 18.0% after 5 min, respectively. As reported by Sumerlin's group,[22] when water was added to the five-member cyclic boronic esters in a 15:1 molar ratio (approximately 15 equiv compared to boronic ester groups), ∼97% of the boronic esters was hydrolyzed after 30 s. We further studied the hydrolytic equilibrium of NCBC-1 and

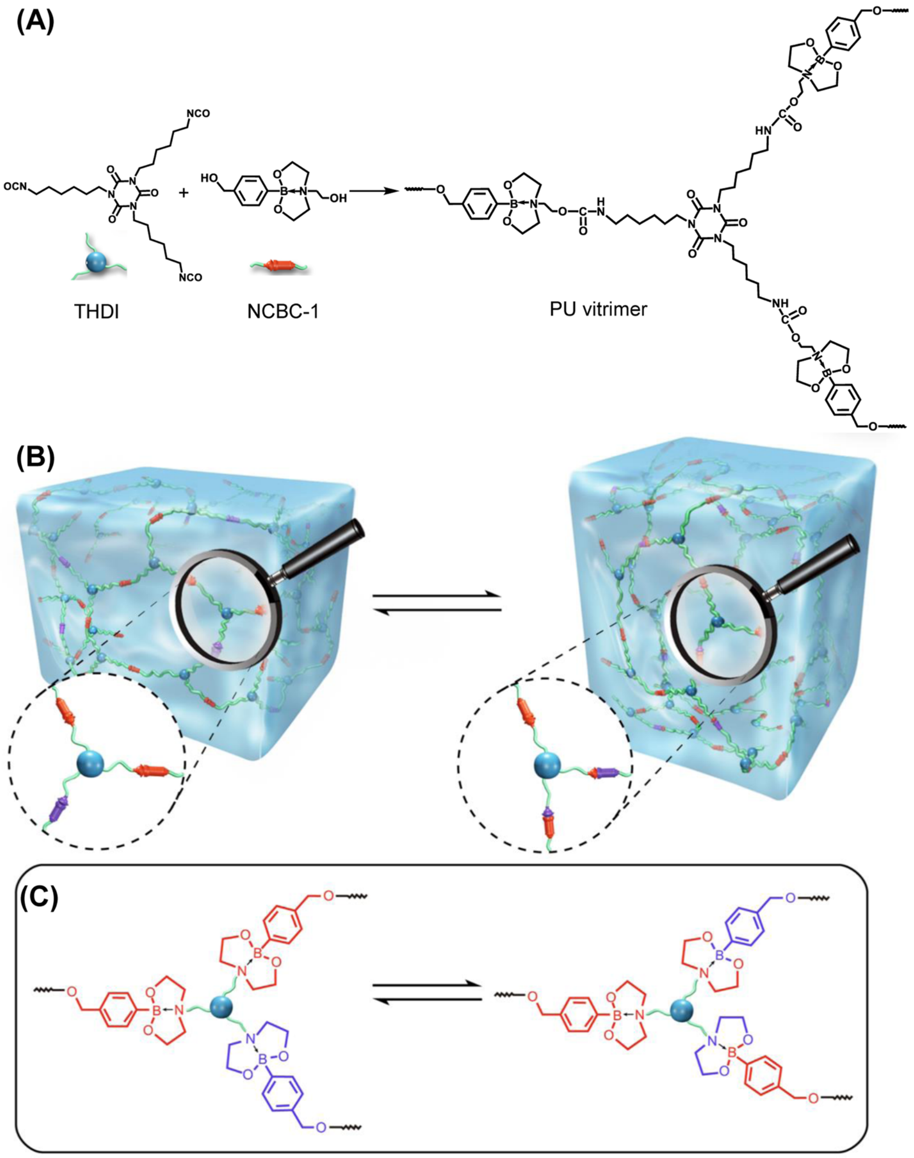


Figure 1. Design concept: (A) Chemical route for the fabrication of PU vitrimers from the reaction of the active hydrogen in NCBC-1 with THDI. (B) Rearrangement of PU networks via associative exchange reactions of NCB linkages. (C) Speculative exchange reactions of NCB linkages in PU networks.

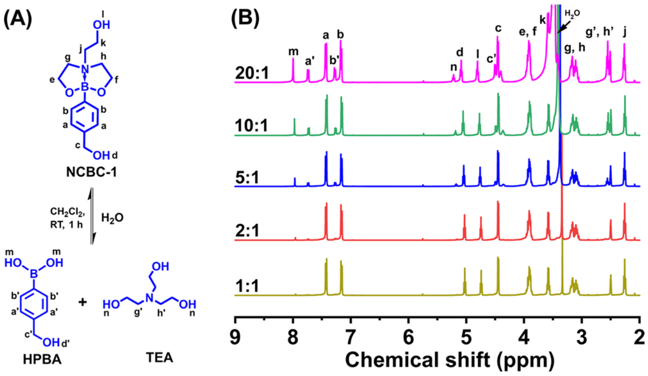


Figure 2. Hydrolytic stability for NCBC-1. (A) Hydrolysis reaction of NCBC-1. (B) ^{1}H NMR spectra of the NCBC-1 in DMSO-d_6 after the addition of different amounts of water at 25 °C for 5 min. The molar ratios of H_2O versus NCBC-1 are 1:1, 2:1, 5:1, 10:1, and 20:1, respectively.

NCBC-2 at a fixed water concentration and obtained the hydrolysis equilibrium constant (K_{eq} = ([boronic acid] [donor])/[NCBC] $[H_2O]^2$) of NCBCs. The K_{eq} of NCBC-1 and NCBC-2 at 25 °C are 4.78×10^{-3} and 3.67×10^{-3} L·mol^{-1}, respectively, which is significantly lower than that of the five-member cyclic boronic ester reported in the reference.[35]

Furthermore, the model compounds containing urethane group and urea group were synthesized by reacting NCBC-3 and NCBC-4 with hexyl isocyanate (Schemes S8 and S9 and Figures S14 and S15) and were named as NCBC-X1 and NCBC-X2, respectively. Then their hydrolysis stability was studied by ^{1}H NMR (Figures S16 and S17). NCBC-X1 showed excellent hydrolytic stability as NCBCs and the hydrolysis percentage was 30%, while that for NCBC-X2 was also completely hydrolyzed. The reason is that once NCBCs containing an amine nitrogen atom in NCBCs reacted with the isocyanate, the electron cloud density on the nitrogen atom decreased as the lone pair of electrons on nitrogen was engaged in the formation of the urea

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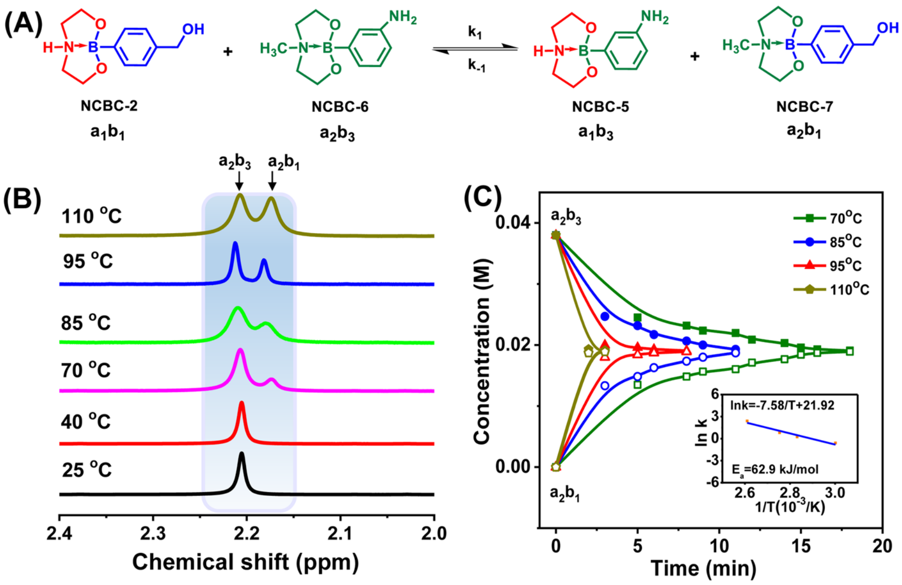

Figure 3. Dynamic exchange reactions between NCB linkages. (A) Transesterification reaction between NCBC-2 and NCBC-6. (B) ^{1}H NMR spectra for the methyl of the mixture of NCBC-2 (a_1b_1) and NCBC-6 (a_2b_3) at variable temperatures. (C) Kinetic data of the transesterification between NCBC-2 (a_1b_1) and NCBC-6 (a_2b_3). The reaction kinetics were plotted as the concentration of the reactant NCBC-6 (a_2b_3) decreased, and the concentration of the product NCBC-7 (a_2b_1) increased with the increase of temperature and time. The inset shows the Arrhenius plot of the logarithm of the reaction rate constant (ln k) versus the reciprocal of the temperature ($1/T$); the E_a calculated from the Arrhenius plot was estimated to be 62.9 kJ/mol. The details of the exchange reaction kinetics are described in the Supporting Information.

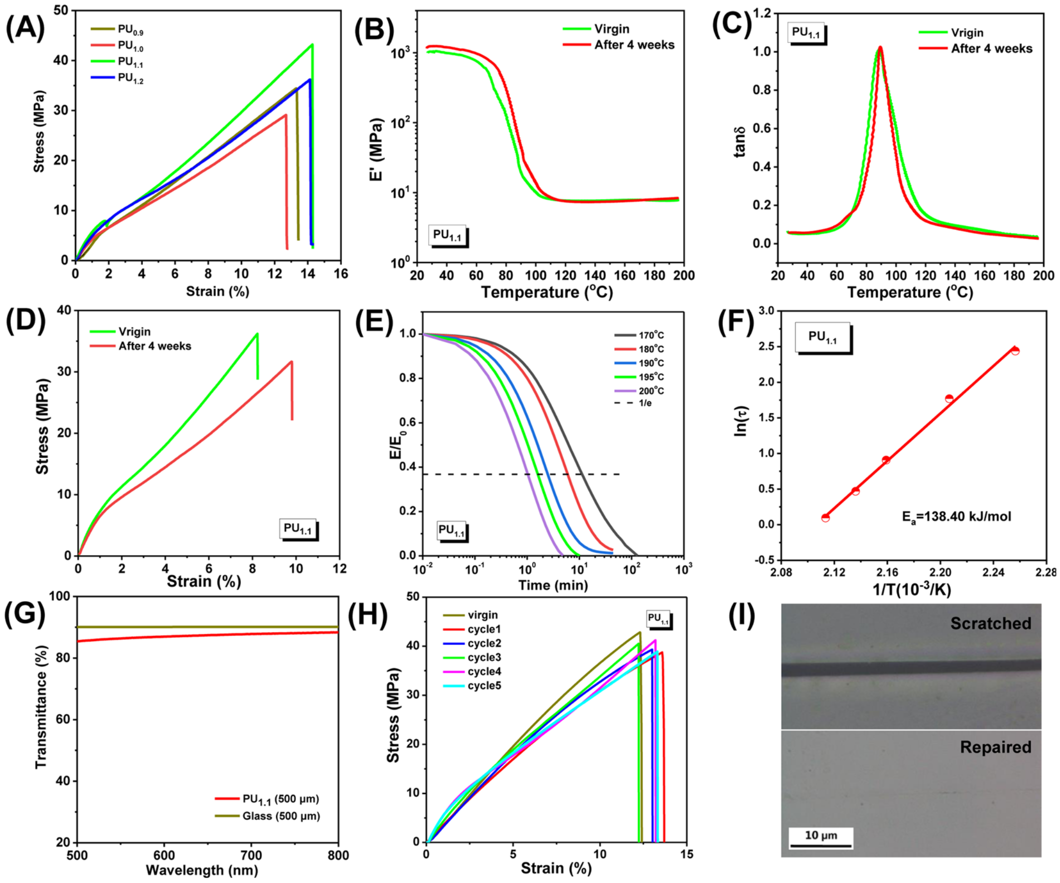

Figure 4. Dynamic nature and superior properties of PU vitrimers based on NCB linkages. (A) Stress−strain curves of PU vitrimers with different stoichiometric ratios. (B)−(D) Storage modulus, tan δ curves, and stress−strain curves of $PU_{1.1}$ after exposure to 40% RH for a certain time. (E) Stress relaxation curves of $PU_{1.1}$ at various temperatures. (F) Linear regression of the logarithm of relaxation time (ln τ) versus the reciprocal of temperature ($1/T$) for $PU_{1.1}$. (G) Visible light spectra of commercial silicate glass and $PU_{1.1}$. (H) Stress−strain curves of virgin and recycled $PU_{1.1}$. (I) Optical microscope images of the scratched and repaired $PU_{1.1}$ coatings at 170 °C for 40 min under a pressure of 10 kPa.

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bond, thus weakening or eliminating the coordination effect of the N → B.

Dynamic Exchange Reactions of NCB Linkages in Model Compounds. Although the N → B coordination makes NCBCs more stable to water, NCB linkages can undergo exchange reactions upon heating without any catalyst. To investigate the dynamic nature of NCB linkages, we first studied the exchange reactions between NCBC and boronic acid (PBA) qualitatively by liquid chromatography (LC). We mixed NCBC-2 (a_1b_1) and PBA (b2) in a 1:1 stoichiometric ratio in anhydrous dimethylformamide (DMF); after the mixture was incubated at 90 °C for 20 min, two new peaks of the target compounds NCBC-4 (a_1b_2) and HPBA (b_1) appeared (Figure S18). The exchange reactions between NCBC-2 and PBA were further studied to obtain the kinetic parameter using variable temperature nuclear magnetic resonance (VT-NMR). Specifically, we mixed NCBC-2 and PBA with a stoichiometric ratio of 1:1 in DMSO-d_6, and the ^{1}H NMR spectra of the mixture were collected every 30 s at certain temperatures until the reaction reached an equilibrium state. According to the Arrhenius equation, the activation energy (E_a) of the reaction between NCBC-2 and PBA was calculated to be 43.6 kJ/mol (Figures S19 and S20). With use of the same method, the E_a for the reaction of NCBC-2 (a_1b_2) with NCBC-6 (a_2b_3) was calculated to be 62.9 kJ/mol (Figure 3, Figure S21); this value was higher than that of the five-membered cyclic boronic ester (15.9 kJ/mol).[12] Thus, because of the stable N → B internal coordination, the exchange rate of the NCB linkages is lower than that of the common cyclic boronic esters.

Synthesis of PU Vitrimers and PUU Vitrimers. After demonstrating the dynamic reversibility of NCB linkages based on small molecules, we set out to construct polymer networks based on NCB linkages. Classical polyurethanes (PUs) or poly(urea-urethane)s (PUUs) were usually synthesized from polyisocyanates with polyols or polyamines. Herein, PU vitrimers and PUU vitrimers based on NCB linkages can be readily assembled from difunctional NCBCs (such as NCBC-1 and NCBC-2) and trifunctional isocyanate (THDI) under mild conditions without any catalyst; the general schemes of PU vitrimers and PUU vitrimers are depicted in Figure 1A and Scheme S10, respectively.

Considering the deviation between theoretical and actual values resulting from the purity of the reagents, PU vitrimers and PUU vitrimers with different stoichiometric ratios were synthesized. The cross-linked structures of PU vitrimers and PUU vitrimers were confirmed by FTIR (Figure S22) and swelling tests. PU vitrimers and PUU vitrimers showed good chemical resistance and are insoluble but swollen in DMF and other polar solvents (Figure S23 and Tables S15−S17), indicating that the integrity of the cross-linked structure was maintained even when heated. PU vitrimers and PUU vitrimers with different stoichiometric ratios exhibited different thermal properties (Figures S24−S26 and Table S18). $PU_{1.1}$ and $PUU_{1.1}$ showed the highest glass transition temperature (T_g, 87 and 78 °C, respectively) and thermal decomposition temperature ($T_{5\%}$, 215 and 228 °C, respectively) among samples with different stoichiometric ratios, indicating that a relatively complete reaction occurred in the corresponding reactants ratio.

Mechanical Properties and Water Resistance of PU Vitrimers and PUU Vitrimers. PU vitrimers and PUU vitrimers showed good processability as the pulverized resin can be reprocessed by means of compression molding at high temperatures. As expected, PU vitrimers and PUU vitrimers exhibited excellent mechanical properties. For example, the tensile strengths of $PU_{1.1}$ and $PUU_{1.1}$ are 43.0 and 36.7 MPa, respectively (Figure 4A and Figure S27), which are superior to those of most reported PU materials with a dynamic covalent network.[36−40]

Generally, the boronic ester linkages are easily hydrolyzed and the corresponding materials exhibit poor water resistance. Because of the N → B internal coordination of NCB linkages, PU vitrimers showed significantly improved water resistance. We confirmed this by exposing the bulk $PU_{1.1}$ to the environment with a constant temperature and humidity. There was almost no decrease in the T_g and mechanical properties for PU vitrimers, even after exposure to 40% RH at 30 °C for 4 weeks (Figure 4B−D; Figure S28). These results are in agreement with those described in model NCBCs. This is a breakthrough of the dynamic cross-linked polymers based on the boronic ester linkages. Surprisingly, despite the fact that the small molecule of NCBC-X2 is easy to hydrolyze, the T_g and mechanical properties of $PUU_{1.1}$ did not significantly reduce after exposure to 40% RH at 30 °C for 4 weeks (Figure S29). We believe that the cross-linking networks of the polymers can prevent water molecules, thereby inhibiting hydrolysis of the boronic esters.

Considering the potential applications for PU vitrimers and PUU vitrimers based on NCB linkages, the hydrolytic stability of the vitrimers was further investigated by immersing $PU_{1.1}$ and $PUU_{1.1}$ samples in distilled water. After 7 days at room temperature (25 ± 3 °C), the overall appearance of the $PU_{1.1}$ samples remained almost unchanged, while that for the $PUU_{1.1}$ sample partially paled (Figure S30). The water uptake of $PU_{1.1}$ and $PUU_{1.1}$ was 3.4% and 8.9% (Tables S19 and S20), respectively, under the same conditions.

Although the breaking strength and Young's modulus of $PU_{1.1}$ and $PUU_{1.1}$ decreased slightly compared to those of the original samples after immersion in water for a period of time (Figure S31 and Table S21), one can obviously observe that $PU_{1.1}$'s water resistance was superior to that of $PUU_{1.1}$ because of the difference in the stability of NCB linkages embedded in the polymer networks. In fact, because the large number of urethane groups and/or urea groups existed in the $PU_{1.1}$ and $PUU_{1.1}$, the higher water absorption and plasticization of which had a significant impact on the mechanical properties. Even then, the water resistance of $PU_{1.1}$ and $PUU_{1.1}$ is still superior to that of dynamic cross-linked polymers based on conventional boronic esters and boroxine linkages.[11,28] When the NCB linkages are introduced into the relatively hydrophobic polystyrene (PS) skeleton (Scheme S11), the water resistance of the NCB linkages can be fully utilized. After immersion in water for 24 h (25 ± 3 °C), the breaking strength and Young's modulus of NCB based PS vitrimer can still maintain 90% of the original sample (Figure S32 and Table S21). This is consistent with the results reported by Guan et al.[26] Furthermore, PU vitrimers can maintain the structural integrity, even after immersion in boiling water. $PU_{1.1}$ can maintain the structural integrity after being boiled in water at 80 °C for 8 h (Figure S33a). After drying (100 °C, 12 h), the appearance of $PU_{1.1}$ was restored to the original sample, and the mechanical properties only slightly decreased (Figure S33b). For example, the breaking strengths of $PU_{1.1}$ before and after in immersion in boiling water and drying were 54.47 and 49.34 MPa, respectively (Table S22).

Stress Relaxation Behavior of PU Vitrimers and PUU Vitrimers. The viscoelasticity properties of PU vitrimers and PUU vitrimers were studied by stress relaxation tests. Full stress

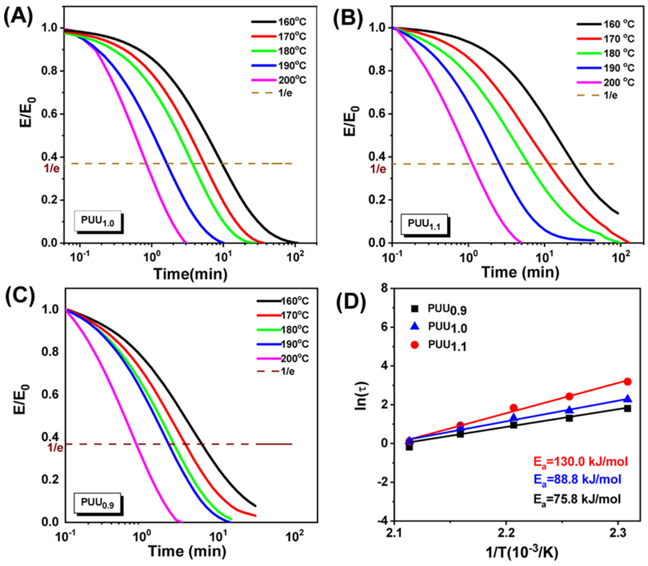

Figure 5. (A)−(C) Stress relaxation curves at various temperatures for PUU vitrimers. (D) Linear regression of the logarithm of relaxation time ln(τ) versus reciprocal of temperature ($1/T$) for PUU vitrimers.

relaxation was observed at high temperatures despite the high cross-linking structure of PU vitrimers and PUU vitrimers (Figure 4E, Figure 5, and Figure S34), which confirmed the malleability of PU vitrimers and PUU vitrimers. The relaxation time (τ) rapidly decreased with increasing temperatures for PU vitrimers and PUU vitrimers. Because of the associative exchange mechanism of the NCB linkages, the relationship between τ and temperatures for PU vitrimers and PUU vitrimers can be well described by the Arrhenius equation (Figure 4F, Figure S34b,d, and Figure 5d). E_a for PU vitrimers and PUU vitrimers can be obtained according to the linear correlation of ln(τ) with $1/T$. Because of the high stability of NCB linkages, the E_a values for PU$_{1.1}$ and PUU$_{1.1}$ were 138.4 and 130.0 kJ/mol, respectively, which were much higher than those of vitrimers based on conventional boronic esters (76.7 kJ/mol) and boroxine linkages (79.5 kJ/mol).[30,41] It can be seen that vitrimers based on NCB linkages show not only good hydrolytic stability but also good heat resistance (such as higher E_a) as compared to other dynamic cross-linked polymers based on conventional boronic esters, which greatly expands the application of this kind of material. To further prove the integrity of the cross-linked structure of NCB-based vitrimers at high temperatures, we used a dynamic thermomechanical analyzer and rheometer to conduct frequency sweep experiments and temperature sweep experiments for PU$_{1.1}$ and PUU$_{1.1}$, respectively. The results showed that the PU$_{1.1}$ and PUU$_{1.1}$ at different temperatures did not exhibit a significant decline in storage modulus, indicating that the cross-linking density of the vitrimers remained unchanged at different temperatures (Figures S35−S37).

We propose that the full range of the vitrimers' stress relaxation behaviors are primarily affected by temperature and a small number of impurities, such as water, boronic acid, or other hydroxyl-containing compounds. Compared to PU$_{1.1}$, there may be some residual hydroxyl groups in the PU$_{1.0}$ and PU$_{0.9}$ networks, which are conducive to the exchange reactions of the NCB linkages. The stress relaxation results support our hypothesis. As shown in Table S23, the E_a's of PU$_{1.0}$ and PU$_{0.9}$ were significantly lower than that of PU$_{1.1}$; this trend was also applied to the PUU vitrimers.

In addition to T_g, T_v is another key characteristic for vitrimers, as it corresponds to the transition from the viscoelastic solid to the viscoelastic liquid resulting from the exchange reactions within the polymeric network. Conventionally, T_v for vitrimers is considered the temperature at which the viscosity reaches 10^{12} Pa·s;[42−46] accordingly, T_v values for PU$_{1.1}$ and PUU$_{1.1}$ were calculated to be 110 and 107 °C (details are shown in the Supporting Information). As the temperature increased to T_v, the exchange reactions of NCB linkages became fast. Once the concentration of the exchangeable dynamic covalent bonds reached a certain threshold, the rearrangement of cross-linked networks became possible and the macroscopic flows occurred in vitrimers; ultimately, the vitrimers can be reprocessed and recycled.

Reprocessing and Recycling of PU Vitrimers and PUU Vitrimers. It is known that vitrimers can be reprocessed, repaired, and recycled at high temperatures, while still maintaining a relatively constant cross-linking density thanks to the associative exchange reactions. As expected, solid-phase reprocessing and liquid-phase recycling of PU vitrimers and PUU vitrimers can be realized via the exchange reactions of NCB linkages upon heating without any catalyst, and the multiple reprocessed and recycled vitrimers showed mechanical properties similar to the virgin materials.

The reprocessability of PU vitrimers and PUU vitrimers was investigated by compression molding. The specific reprocessing procedure is shown in Figure 6A. The reprocessed bulks were uniformly transparent with the transmittance above 80% in the visible wavelength range (Figure 4G). The structure of PU vitrimers and PUU vitrimers showed no obvious change over five reprocessing cycles (Figure S38). The T_g's of reprocessed PU$_{1.1}$ were almost equal to that of the virgin sample (Figure S39). Furthermore, there was no evident decrease in tensile strength, Young's modulus, or elongation at break after being reprocessed five times (Figure 4H and Figures S40 and S41). Therefore, because of the exchange reactions among the NCB linkages, the network rearrangement and bond reshuffling occurred, enabling the PU networks and PUU networks to be reshaped and reprocessed in a solid state at high temperatures. However, this solid-phase recycling method is somewhat limited, especially for the resin−matrix composites, as damages on the reinforced fibers will be unavoidably produced.

In this work, we proposed a more useful recovery method as presented in Figure 6B. Taking PU$_{1.1}$ as an example, in essence, the chemical equilibrium of the cross-linked network can be completely destroyed by the exchange reactions induced by adding excessive TEA or HPBA; then PU vitrimers can be fully recycled to their oligomers. After the addition of 3 equiv of TEA, the NCB linkages in the PU network were broken as a result of the exchange reactions upon heating. When the number of cross-links decreased to the percolation threshold, the PU vitrimer could be fully dissolved and returned to the liquid state. After the addition of 3 equiv of THDI and 3 equiv of HPBA, the resin could be recurred through the reaction between active hydrogen atoms and isocyanate groups. The structure and mechanical properties of the recycled PU$_{1.1}$ and PUU$_{1.1}$ were considerable to those of the virgin samples (Figures S42 and S43). This method is highly significant for the complete recovery of the matrix resin and the expensive carbon fiber from resin−matrix composites without sacrificing their commercial use and value.

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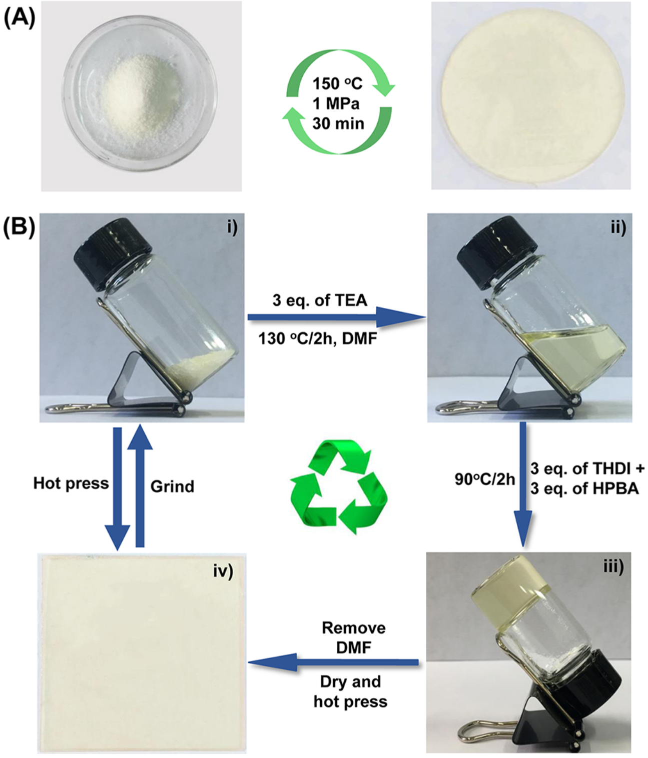

Figure 6. Reprocessing and recycling processes of PU vitrimers. (A) Reprocessing of $PU_{1.1}$ powders (left) by compression molding to reform the bulk material (right, after the fifth cycle) at 150 °C and 1 MPa. (B) Recycling process of PU vitrimers. (i) PU bulks were ground into powders. (ii) Powders were dissolved in DMF and treated with 3 equiv of TEA at 130 °C for 2 h. (iii) Reformation of PU network by adding 3 equiv of THDI and 3 equiv of HPBA incubated at 90 °C for 2 h. (iv) Recycled square-shaped PU sample via hot-pressing of the reformed PU after pulverization and vacuum-drying treatment.

PU vitrimers and PUU vitrimers can be used to prepare remendable adhesives and coatings through the NCB exchange-induced network rearrangement. As the raw material NCBC-1 for PU vitrimers showed good solubility, PU adhesive and coating were prepared and their repairable properties were studied. As shown in Figure S44, the PU adhesive can be easily repaired by heating it to 170 °C under 0.5 MPa, as this condition will activate the exchange reactions of NCB linkages. The repaired adhesive's lap-shear strength showed no significant decrease compared to that of the pristine sample (Figure S44e). A scratch on the $PU_{1.1}$ coating can be repaired by heating it at 170 °C for 20 min under a pressure of 10 kPa because of the reformation of covalent bonds across the interfaces. The obtained $PU_{1.1}$ coating showed good adhesion (Grade 0) and flexibility (1 mm). Optical microscopy images of PU coating are described in Figure 4I.

CONCLUSION

In summary, based on the principle that the nitrogen-donor compounds can "lock" the vacant orbital of the boron atom to stabilize the boronic ester linkages, we studied the chemistry of NCB linkages and fabricated the PU vitrimers and PUU vitrimers with enhanced stability based on NCB linkages. NCBCs showed high hydrolytic stability but still undergo transesterification upon heating without any catalyst. The NCBC-X1 containing urethane group also showed excellent hydrolytic stability like NCBCs, even higher than conventional boronic esters. Both PU vitrimers and PUU vitrimers exhibited excellent solvent resistance and mechanical properties like general thermosets, solid-phase reprocessing of PU vitrimers and PUU vitrimers can be achieved via the transesterification of NCB linkages upon heating. Besides, reversible conversion between the oligomer and polymers can also be realized by the exchange reactions among NCB linkages; the multiple reprocessed and recycled vitrimers showed mechanical properties similar to the virgin samples. Moreover, NCB-based vitrimers showed enhanced water and heat resistance as a result of the highly hydrophobic structure of the NCB linkages, in which there was almost no decrease in T_g or mechanical properties when exposed to 40% relative humidity at 30 °C for 4 weeks. This study provides a novel chemical strategy and concept for designing a range of robust and stable vitrimers with the potential for commercial industrial applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10244.

X-ray crystallographic data of NCBC-1 (CIF)
X-ray crystallographic data of NCBC-2 (CIF)
X-ray crystallographic data of NCBC-3 (CIF)
X-ray crystallographic data of NCBC-4 (CIF)
All experimental details including synthesis and characterizations, model reaction, polymerization, sample preparation, and mechanical studies (PDF)

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Notes

The authors declare no competing financial interest.

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