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Simple Approach for a Self-Healable and Stiff Polymer Network from Iminoboronate-Based Boroxine Chemistry

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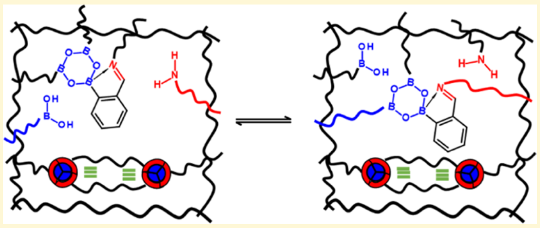
Supporting Information



ABSTRACT: Despite offering robust mechanical properties, polymer networks suffer from a lack of recyclability, reshaping, and healability. Designing stiff and remendable polymer networks that can repair under mild conditions remains a challenge to extend their field of applications. Herein, we describe a simple approach to design a nonisocyanate-based polyurethane network featuring multiresponsiveness (to humidity and temperature) and outstanding healing properties, as obtained by combining iminoboronate and boroxine chemistry. In spite of the presence of abundant dynamic bonds, the network has a high stiffness (Young's modulus of 551 MPa) and tensile strength (11 MPa). C═N iminoboronate and B−O boroxine exchange reactions at high temperature enable efficient network recycling over multiple cycles without compromising its properties. Owing to these features, 3D objects could be designed and printed. The present approach provides excellent sustainable and high-performance substitution to conventional polyurethane networks requiring the use of toxic isocyanates.

1. INTRODUCTION

Since more than two decades, scientists actively focus on the development of polymers that are able to react to a damage and heal during their use in various applications. This familiar concept, known as self-healing, is derived directly from living organisms; materials exhibiting this intrinsic resource would see their service life prolonged, hence reducing production costs.[1−5] Transferring such properties into a material has been made possible by different approaches. Pioneering works led to extrinsic self-healing materials, in which a healing agent of a nature different from that of the polymer matrix (e.g., microcapsules) is encapsulated.[6−8] Intrinsic self-healing properties were then introduced, allowing the polymer matrix to repair itself by utilizing intrinsically dynamic supramolecular interactions (hydrogen bonding,[9−12] metal−ligand interactions,[13−18] ionic interactions,[19−21] $\pi-\pi$ stacking interactions[22−24]) or specific covalent bonds that can be reversibly formed or suppressed (disulfide,[25,26] B−O boronic ester[27−29] or boroxine,[30,31] Schiff base,[32−34] Diels−Alder reaction[35−37]), via a trigger. Although being the most widely studied, intrinsic self-healing approaches reported to date do not perfectly fulfill the requirements for industrial applications, as they cannot reconcile straightforward fabrication with high mechanical performance and autonomous self-healing abilities.

Thermosets yield high mechanical and thermal performances for many applications such as coatings, adhesives, or composites.[38−42] These properties are driven by the cross-linking of polymer chains, hindering their melting reprocessability and therefore making them nonsustainable. Introducing reversible cross-linking has been shown as an attractive solution for the design of self-healing and recyclable thermosets. Among them, cross-linked polyurethanes (PUs) are widely produced and consumed worldwide. The latter are generally synthesized using a wide range of polyols and polyisocyanates though isocyanate compounds are toxic and raise health, handling, and environmental concerns. Therefore, as an alternative, nonisocyanate PU (NIPU) thermosets have gained a high interest. They are obtained mostly by step-growth polymerization of multi-amines with multi five- or six-membered cyclocarbonates, leading to polyhydroxyurethane (PHU) networks.[43] So far, only few studies report recyclable, reprocessable, and healable NIPUs. A PHU vitrimer has been recycled at $T > 160$ °C via a transcarbamoylation process occurring without any additional catalyst.[44] The Caillol's group developed thermoreversible and reprocessable NIPU by converting furfuryl glycidyl ether into cyclocarbonate derivative and mixing it with dimaleimide-terminated polypropylene glycol and appropriate diamine.[45] Recently, Chen and co-

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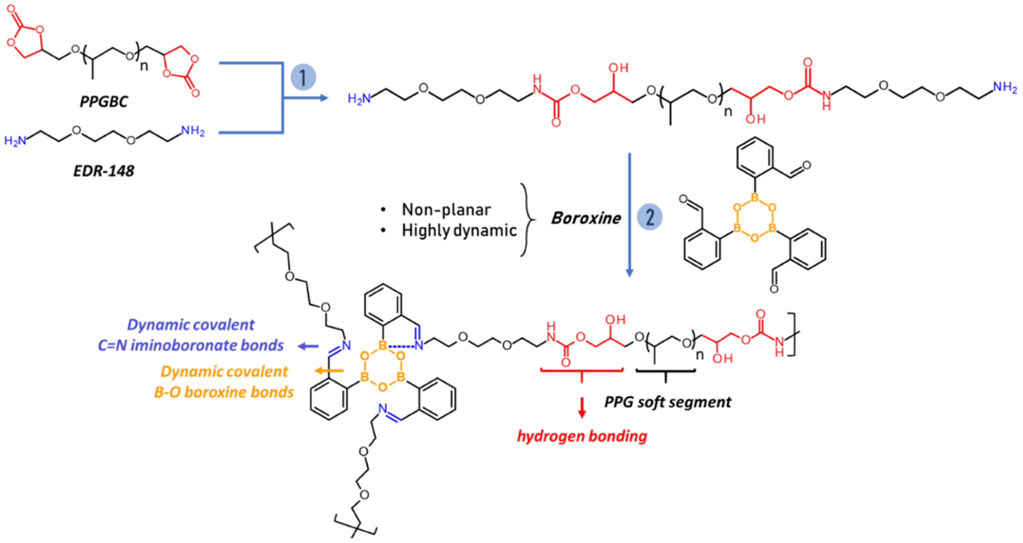
Scheme 1. Synthesis of the Prepolymer and the Iminoboronate/Boxorine-Based PU Network



workers discovered that the presence of dimethylaminopyridine as a catalyst in PHU leads to dynamic and reprocessable networks through transcarbamoylation and reversible cyclic carbonate aminolysis.[46] On a similar track, reprocessable NIPUs were obtained by reacting cyclocarbonate end-functionalized acetal-containing dendrimers with commercial diamines.[47] Advantageously, the material can be reprocessed under acid catalysis thanks to its acetal functions, reversibly regenerating diol, and aldehyde functions. However, for these systems, the need for a catalyst and/or high temperature for the polymer to recycle as well as the number of steps required for the polymer fabrication often constitutes serious hurdles and reduces therefore their applicability.

In a recent work, we have exploited the iminoboronate-based boroxine chemistry for the design of ambient humidity-sensitive self-healing polymers.[31] Taking advantage of the water-driven dynamic boroxine/boronic acid equilibrium and iminoboronate chemistry as linker between polymer chains and dynamic nodes, it was possible to obtain polymeric materials that are able to self-heal via the B−O dynamic bonds without requiring any energy-demanding external activation. Interestingly, this novel family of iminoboronate adduct-based materials could be readily produced by a relatively simple synthesis between boronic acid anhydride and diamine-based compounds. In the present work, we envisioned an original combination between our iminoboronate/boroxine system and the cyclocarbonate chemistry to enhance the mechanical properties of our previous polymer and obtain a stiff yet easily healable material designed through a straightforward process. We found out that we can produce multistimuli responsive NIPU networks by simply using commercial amino-, cyclocarbonate- and deshydrated boronic acid-based compounds. Under ambient conditions, the dynamic aspect is governed by humidity thanks to the boroxine reversibility, yielding a high mechanical modularity from rigid to flexible materials with reshaping abilities as well as humidity-induced healing properties. At high temperature ($T > 70$ °C), B−O boroxine and C═N iminoboronate bonds can simultaneously undergo exchange reactions, enabling extremely fast stress dissipation and complete reprocessing of the material. Moreover, the polymer can rapidly switch from a glassy state to a viscous liquid when heated up at the exchange reaction temperature, making it convenient to design tridimensional objects. This unique and simple approach therefore allows for the fabrication of stiff, dually responsive, self-healable, reshapable, and reprocessable nonisocyanate based PU networks with high mechanical performance.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Boroxine/Iminoboronate-Based Cross-linked NIPU Networks. The boroxine/iminoboronate-based cross-linked NIPUs are prepared from commercially available products (polypropylene glycol bis carbonate 640 g·mol^{-1}—PPGBC and 1,8-diamino-3,6-dioxaoctane—Jeffamine EDR-148) and presynthetized 2-formylphenylboronic acid anhydride—2FBA anhydride. In a first step, EDR-148 and PPGBC are mixed to prepare amino-telechelic poly(propylene glycol) (PPG)-based hydroxyurethane precursor (prepolymer—see Scheme 1 and Figure S1 in the Supporting Information). An overall excess of amino groups ensures the complete consumption of cyclocarbonate, which remains a current problem during the synthesis of NIPU networks.[48] Moreover, the excess of EDR-148 also ensures that no chain coupling is occurring during the end-chain functionalization as demonstrated by matrix-assisted laser desorption ionization time-of-flight analysis (Figure S1b). In a second step, 2-FBA anhydride is added, and the material is cured until complete solvent removal at 70 °C. The properties of the boroxine-based NIPUs could be readily tuned by the molar ratio PPGBC/2-FBA, keeping the ratio NH_2/(cyclocarbonate + aldehyde) equal to 1 (compositions summarized in Table S1 in the Supporting Information). The formation of the networks was confirmed by attenuated total reflection−Fourier transform infrared highlighting the presence of characteristic hydroxyurethane and boroxine bonds (see Figure S2 in the Supporting Information). Density functional theory (DFT) calculations were performed with the B3LYP functional and a 6-31G-(d,p) basis set to support our choice for 2-formylphenylboronic acid as boroxine precursor to obtain good self-healing properties. Boroxines are known to generally exhibit an aromatic character because of the boron−oxygen alternation in the heterocycle.[49−51] When connected to a phenyl group, the extended conjugation in the molecule affords an increased stability to the resulting phenylboroxine. Never-

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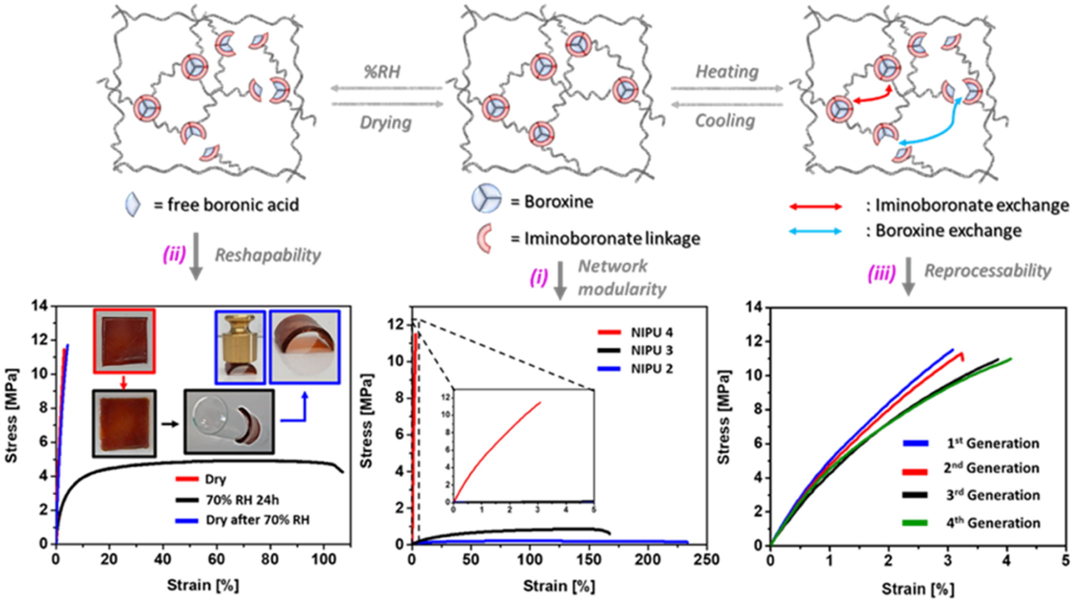


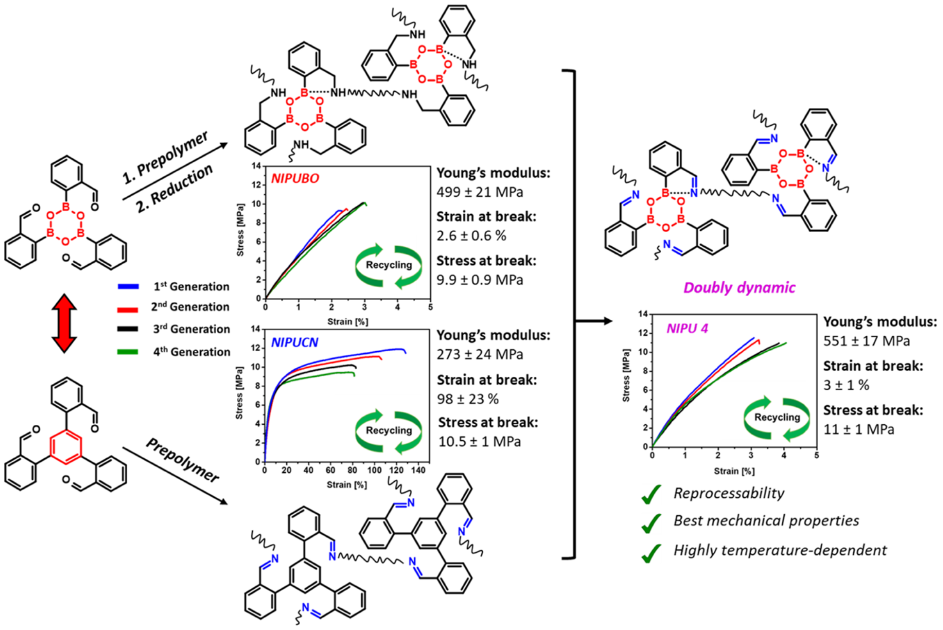
Figure 1. Schematic structure of the polymer showing: (i) the modularity and mechanical performance for each composition of the NIPU networks, (ii) the moisture-induced malleability of the **NIPU 4** network with characteristic stress−strain curves; pictures show that the polymer can be reshaped after 70% RH exposure and can support a load of 100 times its own weight after drying; and (iii) the recyclability of the **NIPU 4** network when heated, engaging two different mechanisms of exchange.

theless, the DFT results show that 2-FBA anhydride is nonplanar, with a twist angle of 17.43° between the phenyl and boroxine rings (see Figure S3a in the Supporting Information). The carbonyl groups present in ortho position actually make the formation of boroxine difficult because of steric hindrance,[52] which entails a twisted structure when the boroxine synthesis is forced. Additionally, these carbonyl groups make the boron centers electron deficient because of their electron-withdrawing character, hence enhancing the boroxine reactivity toward nucleophilic species such as water and making the cleavage/formation of the structure highly dynamic and well suitable for the self-healable ability. Infrared spectroscopy data performed at 50% relative humidity (HR) support this picture when comparison is made with the hydrolysis rate of a more planar and stable phenylboroxine compound (see Figure S3b in the Supporting Information). On the other hand, the iminoboronate bond is created by an imine that interacts through its nitrogen-atom lone pair with an electron-deficient boron, located here in the boroxine.[53,54] Another key parameter is thus the N−B coordination conjugation level. Theoretical calculations on model compounds show that structures with one or two dative bonds out of the three possible are the most favorable (see Figure S3c in the Supporting Information). When one coordination is established, the more stable configuration yields a N−B bond of 1.66 Å long. This structure is thermodynamically more stable (by 3.31 kcal/mol) than the one with two N−B dative bonds, with N−B lengths of 1.71 Å for both. These results are fully consistent with previously reported boron NMR experiments obtained on these iminoboronate model adducts.[31] It is well known that the formation of N−B coordination between boroxine, with boron atoms acting as Lewis acid, and a Lewis base is very beneficial for the boroxine ring construction.[55−57] The N−B bond creation in the single-coordinated adduct **1** (see Figure S3c in the Supporting Information) modifies the $O-B_1-O$ bond angle, switching from 118° in 2-FBA anhydride (sp^2-like hybridation) to 114° (sp^3-like hybridation). $O-B_2-O$ and $O-B_3-O$ bond angles in **1** are 119.5°, representing sp^2-hybridized boron centers. The coordination of B_1 by the nitrogen ligand also results in the lengthening of the B_1-O bond length. Indeed, the B_1-O bond length in **1** is 1.45 Å, whereas the average B−O bond length in 2-FBA anhydride as well as noncoordinated B_2-O and B_3-O bond lengths in **1** is 1.38 Å. These results are in good agreement with previous theoretical studies focusing on boroxine coordination levels.[58,59] The larger deviation from planarity obtained when the boroxine is coordinated makes the heterocycle as a whole more reactive and hence the cleavage more favorable. High reversion possibilities of the boroxine/boronic acid equilibrium are therefore conferred by the intramolecular coordination, which render the system very attractive for intrinsic self-healing properties under mild conditions.

2.2. Modularity and Mechanical Properties of the NIPU Networks. A high modularity of mechanical properties was triggered by varying the boroxine content from 0 to 75% molar [**NIPU 1−4**; see Figure 1(i) and Table S1 in the Supporting Information]. While **NIPU 2** and **NIPU 3**, which contain, respectively, 25 and 50% molar boroxine, behave as soft elastomers (see Table S2 in the Supporting Information), **NIPU 4** exhibits simultaneously a high stiffness (551 MPa for Young's modulus) and strength (3% and 11 MPa respectively for strain and stress at break). Fully PPG-based material (**NIPU 1**) is a viscous liquid and a brittle film was obtained when a fully boroxine-based composition was tested. Tensile tests were therefore limited for these materials. **NIPU 4** is a good alternative to most of soft and stretchable self-healing materials with a high segmental mobility allowing chains to diffuse to polymer/polymer interfaces. Compared with previously reported self-healing designs based on boroxine adducts,[30,31,58] our material is stronger and stiffer (see Table S3 in the Supporting Information). The presence of hydroxyurethanes within the network is expected to provide additional hydrogen bonding interactions and preserve the material for extensive fluidification upon boroxine hydrolytic cleavage.[60,61] The role of these cohesive interactions in the PHU was highlighted by dynamic mechanical analysis, comparing **NIPU 4** with a network containing no hydroxyurethane functions. $H_2N-PPG-NH_2$ (400 g·mol^{-1}) was selected to directly react with 2-FBA anhydride for that purpose, keeping the boroxine percentage in weight unchanged in the network (i.e., 39%).[31] A higher value of storage modulus at room temperature was obtained for **NIPU 4**, showing the beneficial effect of the hydrogen bonding on the network stability and mechanical performance (see Figure S4 in the Supporting Information). Hydrolytic cleavage of boroxine reduces the number of cross-linking nodes with formation of tethered and free boronic acid-terminated chains with high mobility, inducing in turn a softening and malleability of the network [see Figure 1(ii) and Table S4 in the Supporting Information]; the boroxine ring can be reversibly reformed upon water removal.[62] The 70% RH used for softening was shown to induce desired effects in a reasonable and appropriate timescale. Indeed, when exposed at 45% RH for 48 h, the mechanical properties of the polymer were not strongly affected compared with an exposure at 70% RH at 16 and 24 h, as a result of the small hydrolyzed amount of boroxine nodes (see Figure S5, Tables S4 and S5 in the Supporting Information). The impact of boroxine hydrolysis was further confirmed by differential scanning calorimetry (see Table S6 in the Supporting Information). Notably, T_g increased with the boroxine content as the material becomes more cross-linked (from **NIPU 1** to **NIPU 4**—third column). Exposure to 70% RH for 24 h at room temperature drastically decreases the T_g of the boroxine-based materials, as observed during the first heating cycle (fourth column). It is worth stressing that T_g after the second heating cycle is higher due to reformation of boroxine after thermal treatment during the first cycle (fifth column). However, the curing time is not sufficient to reform all of the cross-linking nodes and regain the initial T_g values from the third column. Interestingly, re-cross-linking and hardening of films were achieved by placing them in a hermetic container with a drying agent for 6 h at room temperature. Moisture-driven malleability offers a simple way of reshaping at room temperature and with humidity. This was demonstrated on rigid films which, after exposure to humidity (70% HR), could be bended and reshaped around a circular geometry. After 6 h in a dried atmosphere, the polymer retains its new shape. To qualitatively evaluate the integrity of the new shape, a load of 100 g (100 times the weight of the film) was placed on top of the curved sample (average thickness: 3 mm). The curved shape was maintained under loading for 2 h at ambient humidity level (50−60% RH) [see Figure 1(ii)]. Beyond this time, a small deformation of the sample was observed under loading, pointing out to boroxine ring hydrolysis and subsequent de-cross-linking leading to softening.

2.3. Reprocessability of the NIPU Networks. Imine chemistry constitutes one of the most employed strategy to generate reversible covalent bonds in the field of stimuli-responsive polymers. Degenerative bond exchange including imine condensation/hydrolysis and imine metathesis can occur rapidly, making polyimines well suitable for such applications. A recent study carried out by Zhang et al. spotlights the use of imine linkage as an excellent dynamic candidate for the design of water-driven malleable and highly recyclable catalyst-free network.[32] In the present case, coordination between imine nitrogen and boron atom giving the iminoboronate linkage is known to prevent imine from hydrolysis.[53] This approach was experimentally demonstrated on the basis of molecular models by electrospray ionization mass spectrometry (ESI-MS) (see Figure S6a,b in the Supporting Information). Two opposite trends related to hydrolysis were evidenced when comparing classical imine with coordinated iminoboronate species. The absence of features characteristic of iminoboronate hydrolysis in the spectrum confirms that only boroxine cleavage upon hydrolysis is responsible for the change in material properties when exposed to humidity. Along the line of the aforementioned study conducted by Zhang and co-workers, we have next assessed the possibility to obtain recyclable network through iminoboronate exchange. Although it has been already shown that an electron-rich amine may displace a more electron-poor amine residue in iminoboronate species,[63] to the best of our knowledge, no data in the literature reports on exchange among amines of the same kind. We do observe that upon heating, **NIPU 4** can be reprocessed multiple times [see Figure 1(iii)], partly because of iminoboronate exchange reactions. To do so, dried films were cut into small pieces and gathered in a mold for compression molding (10 bars, 10 min, 80 °C). After four recycling cycles, the color of the polymer remains unchanged. Tensile testing of neat and reprocessed **NIPU 4** shows an overall good retention of its mechanical properties. To demonstrate that iminoboronate exchange occurs in the bulk polymer, a small molecular weight model system was studied, with EDR-148 and boronic acid derivatives as reagents. Procedure details for the synthesis of the model compounds (i.e., parent imines AA & BB and mixed imine AB synthesis) are provided in Figure S7a,b in the Supporting Information. The ESI-MS results indicate that efficient C═N exchange occurs very quickly with iminoboronate-based compounds (see Figure S7c in the Supporting Information). Di Stefano and co-workers have shown that imine metathesis occurs at room temperature in the presence of a minute amount of primary amines, as a result of coupled transimination processes.[64] In AA and BB synthesis, EDR-148 was therefore introduced in excess to ensure that the presence of AB is due to transimination and imine metathesis when the parent imines react together; the small remaining amount of amine is representative of the unreacted free amine groups present in the polymer network. Although the ESI-MS analysis supports transimination at room temperature (see Figure S7c in the Supporting Information), the activation of the iminoboronate exchange in the network can only be achieved by heating it above T_g, as exchange reactions are not expected to occur in a glassy state and so that no recyclability can be achieved at room temperature (see Figure S8 in the Supporting Information). Nevertheless, reversible processes associated with imine chemistry do not constitute the sole dynamic part of the polymer. Because the **NIPU 4** network contains 75% molar of boroxine compound, we also envisioned that boroxine exchange can occur in the polymer when heated up, as recently reported elsewhere.[65] The recyclability properties would therefore be associated with B−O boroxine and C═N iminoboronate bond reshuffling. To isolate both contributions of this doubly dynamic system and verify the impact on the recyclability and the mechanical performance of the network, reference materials were built around single C═N classical imine bonds (**NIPUCN**) and single B−O bonds (**NIPUBO**). The same conditions of compression molding as before were used to assess the reprocessability of the reference materials (10 bars, 10 min, 80 °C). For **NIPUCN** preparation, the boroxine ring was typically replaced by a phenyl ring, thus

Scheme 2. Mechanical Properties of the Single- and Double-Dynamic Networks over Four Generations of Reprocessing at 80 °C[a]



[a]C═N imine and B−O boroxine bonds are both shown to be responsible for the remendability of their networks (**NIPUBO** & **NIPUCN**). B−O bonds appear to have a predominant effect on the mechanical and recyclable properties of **NIPU 4**. The double-responsive network is shown to possess the best mechanical performance because of the combination between boroxine and iminoboronate chemistry.

substituting the B−O dynamic bond by C═C partially double nondynamic bond (see Scheme 2). The tri-aldehyde reference compound was therefore synthesized (see Figure S9a for procedure details and Figure S9b for characterization) and reacted with the prepolymer from step 1 in Figure 1 to form the network, with the same molar ratios and conditions used for **NIPU 4** with boroxine. Infrared spectroscopy attests the formation of the imine functions in the network as well as the complete disappearance of the carbonyl band of the pristine material (see Figure S10a in the Supporting Information). The mechanical properties of **NIPU 4** are higher in terms of stiffness compared with **NIPUCN** whose reprocessability through single C═N bond reshuffling is quite good. Small deviations can, however, be observed for the recyclability after three cycles, likely because of the presence of a long polymer chain as linker between the cross-linking nodes instead of small di- or tri-amines (see Scheme 2). An interesting outcome is that **NIPU 4**, polymer containing B−O dynamic bonding, is much stiffer than **NIPUCN** which contains instead non-dynamic C═C. This result was unexpected as a trade-off has usually to be done between dynamicity and mechanical properties when designing intrinsic self-healable polymers.[66,67] We have also synthesized **NIPUBO** by reduction of the iminoboronate functions in **NIPU 4**. **NIPUBO** is very similar to its iminoboronate-based parent material in terms of recyclability and mechanical performance (see Scheme 2). Altogether, the B−O boroxine-based materials studied here display very high mechanical properties with elevated Young's modulus and stress at break as well as outstanding recyclability properties. B−O bonds are basically used as a dynamic functionality, but they also clearly play a role in defining the mechanical performance of the network, as supported by the similar properties of **NIPU 4** and **NIPUBO**. The slight loss in mechanical properties when switching from the former to the latter can be associated with the breakage of C═N strong iminoboronate bond as well as to the competitive hydrogen bonding interactions taking place between hydroxyurethane functions and NH-secondary amine groups formed after reduction. This is supported by infrared spectroscopy with the shift of the urethane band at 1710 cm^{-1} in **NIPU 4** down to 1662 cm^{-1} in **NIPUBO** (see Figure S10b in the ═). The disappearance of the iminoboronate band at 1634 cm^{-1} also confirms that the reduction occurred in the network.

Thermal B−O and C═N exchange reactions were evidenced in **NIPU 4** via stress-relaxation experiments using a rheometer (see Figure 2a and Table S7 in the Supporting Information). To do so, a constant strain of 10% was applied on the sample at different temperatures and the relaxation modulus was followed as a function of time. The results point to a rapid stress-dissipation through the material at different temperatures, characteristic of a network containing exclusively exchangeable cross-links. Moreover, this stress dissipation is extremely fast compared with other works based on exchange reaction in vitrimers,[68,69] as, at 70 °C, the stress is completely dissipated within 20 min. This behavior is likely attributed to the double responsiveness of the network at high temperature through boroxine cross-links and iminoboronate bonds reshuffling. When a NIPU-based network containing only nonexchangeable bonds is considered (**NIPUREF**), most of the initial stress is dissipated by chain motions at elevated temperatures (T_g **NIPUREF** = −21 °C), but a plateau is reached within 1 h (see Figure S11 and Table S8 in the Supporting Information), typical of a network without inherent dynamics; the remaining stored stress cannot be dissipated by the nonremendable network. The synthesis and characterization of **NIPUREF** are depicted in Figure S12a,b in the Supporting Information.

2.4. Self-Healing Efficiency of the NIPU Networks. The healing efficiency of the NIPU networks was then assessed. First, healing of the dually responsive network via moisture was

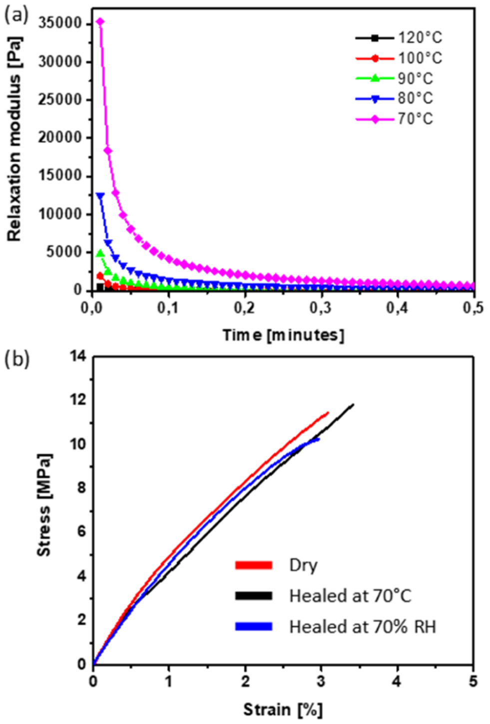


Figure 2. Stress relaxation curves of **NIPU 4** at different temperatures under 10% strain [(a)—zoom on first 30 s of the experiment] and self-healing properties of **NIPU 4** when using temperature or humidity as stimulus (b). Complete recovery of the mechanical properties can be observed in both cases.

demonstrated by optical microscopy. Exposure of the damaged film under controlled RH led to self-repair upon boroxine ring cleavage (see Figure S13 in the Supporting Information). When exposed to 45% RH, gentle material softening was observed but no scratch healing could be achieved, whereas rising the humidity level to 70% RH allows for a complete scratch healing within 12 h at room temperature. Requirement of humidity higher than the average atmospheric level enables faster and on-demand humidity healing properties. The control NIPU network (**NIPUREF**) containing nonreversible linkage displays no healing when damaged and exposed to humidity (12 h, 70% RH, room temperature). For **NIPUCN**, a gentle softening can be observed after 12 h exposure at 70% RH at room temperature because of the presence of "classical" imine bonds[32] though no healing was observed. In the same conditions, **NIPUBO** was able to repair thanks to the presence of humidity-sensitive B−O bonds, which further confirm the importance of boroxine reversion to achieve healing when humidity is the stimulus (see Figure S13 in the Supporting Information). Quantitative self-healing was also assessed through tensile testing for **NIPUBO**, **NIPUCN**, and **NIPU 4**. When cut into two pieces and manually reconnected, the samples (average size of 3 cm × 1 cm × 1 mm) were either exposed at 70% RH for 12 h before to be placed in a container containing drying agent for 6 h at RT or directly placed in an oven at 70 °C overnight. While **NIPUBO** was able to repair efficiently via both heating treatment and 70% relative humidity exposure thanks to the B−O boroxine bonds (see Figure S14a in the Supporting Information), **NIPUCN** was only shown to repair from the application of heat (see Figure S14b in the Supporting Information). Indeed, no reconnection could be made when two pieces of **NIPUCN** were brought back together after 12 h exposure at 70% RH as these conditions only induce a slight softening of the polymer (see Figure S13 in the Supporting Information). Then, to discriminate effect on healing of boroxine cleavage alone or in combination with transimination reactions, quantitative healing tests were evaluated from dry **NIPU 4** (see Figure 2b). Both heating treatment and humidity exposure lead to complete recovery of **NIPU 4** properties (see Figure 2b), indicating once more the role of boroxine alone in the material healing which allows for an entire repair under ambient conditions. Here, the combination of boroxine ring and iminoboronate function therefore constitutes a simple method, with no need of complex derivatization, to meet both superior mechanical resistance and high healing efficiencies widely sought-after nowadays for intrinsic self-healing.

2.5. NIPU 4 at Work.

The highly attractive properties encountered with **NIPU 4** (high mechanical strength; reconfigurable and self-healable via two different stimuli; polymer obtained through a straightforward process) led us to develop a concrete application for the network. The dually responsive polymer was thereby exploited for designing healable tridimensional objects. Previous reports on extrinsic self-healable composite gears highlighted the advantages that such systems could offer compared to metal gears.[70] By taking advantage of the industrial relevance and healing abilities of the network, gear-shaped **NIPU 4** could be designed with the aim of promoting extended service life without seriously damaging the mechanical performance. Corresponding stress-relaxation experiments (see Figure 2a) showed extremely fast stress dissipation at $T > 70$ °C, demonstrating that the polymer can rapidly switch from glassy to viscous liquid state when heated up. Therefore, heating at 80 °C for 12 h pieces of **NIPU 4** into a mold featuring the gear shape led to the desired object with a very good accuracy thanks to the bonds reshuffling and high viscosity drop. The mold was then allowed to cool down at room temperature for 30 min, and a stiff gear-shaped **NIPU 4** of dimensions 6 cm × 6 cm × 3.7 mm was extracted (see Figure 3). Stimuli enabling controlled material response are highly desirable when envisioning such an industrial implementation, as activation of the exchange or healing process must be avoided to prevent loss of mechanical integrity during the service life. It appears that the service temperature is low enough under the polymer T_g to avoid the high exchange reaction rate, keep the structural integrity, and prevent unwanted deformations. Moreover, relative humidity below 45% does not reduce significantly the mechanical performance of the gear, as already shown for tensile specimens (see Figure S5 and Table S5 in the Supporting Information). Complete breakage of a tooth and subsequent healing at 70% RH for 12 h were performed to assess the healing efficiency of the gear (see Figure 3a−b). When inserted for 6 h in a container with a drying agent, the gear could support a load of 100 g (25 times its own weight) with no deformation or disconnection (see Figure 3c). The healing efficiency was also evaluated qualitatively by simulating an operating interconnected gear system (see Figure 3d). A turn of the gear train around three axes of rotation could be easily done without any breakage of the healed tooth. Our intrinsic self-healable system therefore offers efficient repair of the designed object in ambient conditions, with controlled humidity and no need of temperature, thus avoiding unwanted geometric deformations during the remolding.

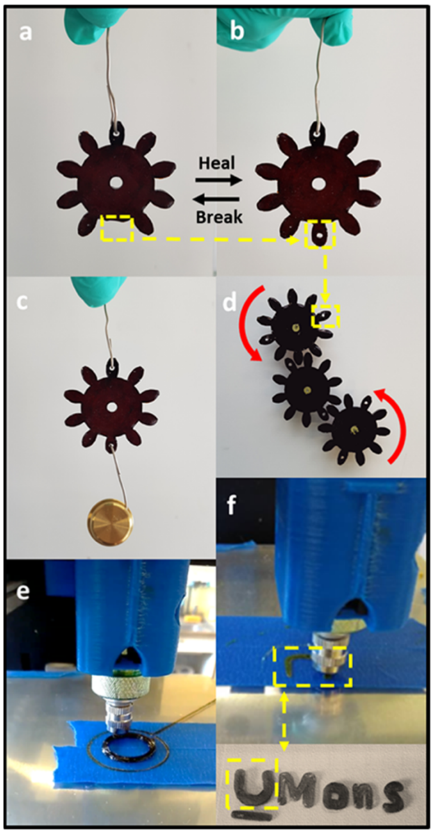


Figure 3. **NIPU 4** with a gear shape. Gear with a fractured tooth (a) and healing of the object at 70% RH at room temperature (b). The gear could support a load of 100 g before and after healing (c) and could be implemented into an interconnected gear system in rotation (d). Printing of simple circular object (e) and UMons logo (f) from **NIPU 4** by fused deposition modeling (FDM).

The highly demanded and currently developed 3D printing process was also tested to create different three-dimensional objects by exploiting the liquid-like behavior of the polymer at high temperature. Compared with classic printable polymers, our polymer has the advantage to self-heal under ambient conditions so that the object does not have to be thrown away if damaged. FDM was selected to print our polymer layer-by-layer. We first printed simple circular objects with low thickness to check the workability of the polymer (see Figure 3e). Encouraged by these results and the accuracy attainable with this method, the logo of the University of Mons was next printed to confirm that the polymer is a good candidate for 3D printing applications (see Figure 3f).

3. CONCLUSION

In summary, we developed a PHU network based on the complementary boroxine and iminoboronate chemistry. This approach permitted not only to afford a sustainable dimension to conventional NIPU networks but also to conciliate mechanical performance and healing efficiency. Dynamic covalent B−O boroxine and C═N imine bond were shown to ensure a high mechanical resistance (Young's modulus up to 550 MPa) of the polymer. Hydroxyurethane functions were successfully added into the network to contribute to the mechanical stability and prevent extensive fluidification of the polymer when exposed to humidity. The multiresponsiveness opens the way to on-demand intrinsic self-healable mechanisms triggered by both temperature or humidity. The stiff **NIPU 4** network is completely healable, reshapable as well as remendable. The machinability of the network was then demonstrated with the formation of rigid and efficiently healable object, induced by non-energy-demanding stimulus (i.e., humidity). Moreover, the method reported here looks very promising for industrial testing as **NIPU 4** could be obtained from a straightforward process, involving only commercially available products. Mechanical and self-healing properties of the NIPUs can be tuned by varying the ratio PPGBC/boroxine, depending on the foreseen application. Further optimizations are still needed, especially in terms of formulation to use our polymer in the printing of more complex objects and ultimately to reach an unlimited degree of freedom for the designed structures.

4. EXPERIMENTAL SECTION

4.1. Prepolymer Synthesis. In a typical experiment for prepolymer synthesis, a total of 2.5 mmol of EDR-148 and PPGBC, with variable EDR/PPGBC ratios (depending upon composition) were mixed in 2 mL of dimethylformamide (DMF) for 48 h at 50 °C. For each composition, EDR-148 was added in excess to ensure the complete consumption of cyclocarbonate.

4.2. NIPU Synthesis. To the solution of the prepolymer was added 2-FBA anhydride to react with the free amino groups, and the medium was then poured into a Teflon mold and cured overnight at 70 °C. The resulting films (**NIPU 1−4**) were finally placed in a ventilated oven at 70 °C for 7 days to remove the traces of the solvent. The fully boroxine-based network (without PPGBC) was directly synthetized by reacting EDR-148 (2.43 mmol) with 2-FBA anhydride (1.61 mmol) in DMF. The medium was then poured into a Teflon mold and cured overnight at 70 °C. The resulting film was finally placed in a ventilated oven at 70 °C for 7 days to remove the traces of the solvent. The **NIPUCN** reference material was prepared under the same conditions than for **NIPU 4** replacing boroxine by 1,3,5-tris-(2-formylphenyl)-benzene reference compound (i.e., PPGBC/tri-aldehyde molar ratio 25:75). The **NIPUBO** reference material was synthetized by reduction of the **NIPU 4** network. Sodium borohydride was used as a soft reducing agent to ensure that only imine functions are reduced, leaving urethane groups intact. In a typical experiment, after preparation of 1 g of **NIPU 4** in solution in methanol (0.292 g EDR-148; 0.315 g PPGTMC; 0.391 g boroxine), sodium borohydride was added in 3:1 molar ratio compared with boroxine (0.11 g—2.9 mmol). The medium was cooled with an ice-water bath during the addition. The reaction mixture was allowed to react during one night at room temperature, after that it was quenched with the addition of water. The salts were removed from DMF extractions, and the solution was poured into a Teflon mold and cured overnight at 70 °C. The resulting **NIPUBO** film was finally placed in a ventilated oven at 70 °C for 7 days to remove the traces of solvent, after what it was ready for further analysis.

Nonremendable reference NIPU (**NIPUREF**) was obtained by replacing 2-FBA anhydride with TMPTC, with the same molar ratio. In a typical experiment, 1 g of **NIPUREF** was prepared by mixing the prepolymer and TMPTC. Prepolymer was synthesized as described above, from 0.282 g (1.9 mmol) of EDR-148 and 0.304 g (0.475 mmol—25%) PPGTMC in DMF. Then, 0.413 g (0.95 mmol—75%) TMPTC was added and the solution was poured into a Teflon mold and cured overnight at 120 °C to ensure conversion of cyclocarbonates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b00750.

Characterization data, mechanical and self-healing studies, and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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