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Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds

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Supporting Information Placeholder

ABSTRACT: Despite numerous strategies involving dynamic covalent bond exchange for dynamic and self-healing materials, it remains a challenge to be able to tune the malleability and selfhealing properties of bulk materials through simple small molecule perturbations. Here we describe the use of kinetically tunable rates of boronic ester transesterification to effectively tune the malleability and self-healing efficiencies of bulk materials. To demonstrate the concept, we used two telechelic di-boronic ester small molecules with variable transesterification kinetics to dynamically crosslink 1,2-diol-containing polymer backbones. We found that the sample crosslinked with fast-exchanging diboronic ester showed enhanced malleability and accelerated healing compared to the slow-exchanging variant under the same conditions. Our report demonstrates the possibility of transferring small molecule exchange kinetics to malleability and self-healing ability of bulk solid material, and may serve as a guide for the bottom-up rational design of tunable dynamic materials.

Polymeric materials that contain reversible bonds and other dynamic interactions exhibit interesting properties, such as adaptability, malleability, and self-healing. In contrast to traditional thermosets, dynamically crosslinked polymers can be reprocessed and recycled while still maintaining their thermal and chemical stability.¹⁻⁶ Moreover, reversible covalent bonds⁷⁻¹¹ and non-covalent bonds¹²⁻¹⁵ have been employed to design selfhealing materials. While many dynamic motifs have been developed for such applications,⁷⁻¹⁵ to our knowledge, systematically tunable motifs whose small molecule kinetics directly correlate to dynamic properties in bulk solid materials largely remain to be explored. Achieving such a goal could aid in the development of novel dynamic materials with tunable properties by simply adjusting the motif's kinetics. Whereas tuning dynamicity of metal-ligand,¹⁶⁻¹⁸ imine metathesis,¹⁹ and protein-ligand²⁰ interactions have been shown to impact various dynamic properties of crosslinked organogels¹⁶⁻¹⁸ and hydrogels²⁰ in solution, such a strategy has rarely been demonstrated in bulk solids for the design of malleable and self-healing materials.²¹

In this study, we used a divalent crosslinker with adjustable exchange kinetics to tune the properties of bulk polymer networks. The dynamics of the functional groups on the small molecule crosslinkers could be kinetically tuned thereby controlling the dynamic and self-healing emergent properties of the resulting networks. In our search for a suitable dynamic motif, the boronic ester bond and its transesterification reaction attracted our attention because of its unique combination of *high thermodynamic stability and kinetic tunability*. The boronic ester

bond has a high bond dissociation energy (B-O bond 124 kcal/mol)²², and, crucially, the rate of boronic ester transesterification can also be tuned over many orders of magnitude with simple neighboring group effects, ranging from effectively inert to extremely fast.²³ Despite these desirable properties, applications for dynamic boronic ester exchange has been largely limited to solution phase,²⁴⁻²⁷ often related to sensing technology for sugars,^{25,28,29} and more recently, for dynamic and self-healing hydrogels.³⁰⁻³² A very recent report described selfhealing bulk material utilizing boronic ester, in which the healing had to be facilitated by water to induce boronic ester hydrolysis and re-formation.³³ No prior report has investigated the tunability of boronic ester exchange kinetics for controlling bulk dynamic properties. We envisioned that the boronic ester transesterification reaction provided an untapped potential as a platform for dynamic material design, allowing us the opportunity to develop of a library of materials with tunable transesterification exchange kinetics and emergent malleability and self-healing properties.



Figure 1. Design concept. **a.** Tuning neighboring group to control the exchange kinetics of boronic ester. **b.** Design of di-boronic ester crosslinkers with tunable exchange kinetics. **c.** Dynamic exchange of boronic ester crosslinkers affords dynamic materials.

Specifically, we demonstrated our concept with a simple polymer embedded with 1,2-diol moieties as attachment sites for boronic esters, crosslinked by telechelic divalent boronic esters. For our initial proof-of-concept, two kinetic variants of di-boronic esters were chosen to serve as dynamically mobile crosslinkers for self-healing (Fig. 1). Consistent with our hypothesis, both crosslinked polymer networks exhibited malleability and reprocessability. However, the two different variants showed variable efficiencies of self-healing, with the faster exchanging linker showing a significant extent of healing at 50 °C, while the slower exchanging linker showed minimal healing. To our knowledge, our report provides the first direct demonstration of tunable malleability and self-healing efficiency through variations in small molecule design.



Figure 2. NMR kinetic study of boronic ester transesterification. **a.** The two model compounds, slower exchanging boronic ester **1** and faster exchanging boronic ester **2**. **b.** EXSY results for compound **1** shows $k = 0.016 \pm 0.004$ /s. **c.** Coalescence for compound **2** shows $k = \sim 3000$ /s.

To confirm that the rate of boronic ester transesterification can be tuned by neighboring groups, we synthesized small molecule model compounds and measured the variable exchange rates in solution.²³ We prepared neopentyl glycol esters from phenyl boronic acid and *o*-(dimethylaminomethyl)phenylboronic acid (compounds 1 and 2, respectively, Fig. 2a), and their rates of self transesterification were monitored in the presence of 1 equivalent excess of neopentyl glycol. The rate of faster-exchanging boronic ester 2 could be monitored through coalescence between bound and unbound glycol methyl resonances in ¹H NMR at varied

Scheme 1. Synthesis of di-boronic ester crosslinkers and 1,2-diol containing polycyclooctene polymer^{*a*}



^{*a*}(a) Synthesis of 'slow' di-phenylboronic ester crosslinker **3**. (b) Synthesis of 'fast' di-*o*-(dimethylaminomethyl) phenylboronic ester crosslinker **4**. (c) Synthesis of 1,2-diol containing polycyclooctene (20%-diol PCO).

temperatures (Fig. 2c).³⁴ The rate of tranesterification was determined to be ~3000/s with an activation energy of 12.6 kcal/mol. The rate of transesterification of the slower exchanging boronic ester **1** could not be monitored through coalescence, and was instead determined via 2D EXchange Spectroscopy (EXSY)³⁵ as 0.016 \pm 0.004/s (Fig. 2b), five orders of magnitude slower than variant **2** which has a neighboring *o*-dimethylaminomethyl group, confirming the earlier observation of strong influence of neighboring group on boronic ester exchange kinetics. It is believed that the nitrogen atom of the *o*-aminomethyl acts as a proximal base to facilitate the proton transfer between the leaving group diol on the boronate and the protonated ammonium during transesterification.^{23,36,37}

We then moved to transfer of this molecular design to dynamically crosslinked polymers. First, di-boronic ester crosslinkers of the slow (**3**) and fast (**4**) variants were synthesized. Crosslinker **3** was synthesized starting from $S_N 2$ substitution of both ends of diethylene glycol with 4-bromobenzyl bromide³⁸ followed by Miyaura coupling with bis(pinacolato)diboron³⁹ to form a telechelic di-boronic ester species. The kinetically inert pinacol esters were deprotected with sodium meta-periodate³⁹ and replaced with the more labile propylene glycol ester⁴⁰ for dynamic crosslinking (Scheme 1a). Faster-exchanging crosslinker **4** was prepared via reductive amination of 2-formyl boronic acid with methylamine followed by nucleophilic substitution of 1,6-dibromohexane, and finally esterification with propylene glycol⁴⁰ (Scheme 1b) (full details in Supporting Information).

We chose to synthesize the 1,2-diol containing polymer backbone using ring-opening metathesis polymerization of cyclooctene-based monomers (ROMP).⁴¹ Dihydroxylated cyclooctene (dHCO) monomer **5** was prepared via stoichometrically controlled epoxidation of cyclooctadiene followed by acid catalyzed epoxide ring opening, which was then copolymerized with cyclooctene to afford 1,2-diol containing polycyclooctene polymer (20%-diol PCO) (Scheme 1c, with full details in Supporting Information.)

Next, we used solution rheology to monitor the solution dynamic properties of polymer networks crosslinked by different boronic ester crosslinkers (Fig. 3a). A solution of 20%-diol PCO in toluene was crosslinked with compound 3 or 4. This caused gelation in sample with crosslinker 3, while the sample crosslinked by **4** showed only a mild increase in viscosity. This is in qualitative agreement with the small molecule exchange kinetics (Fig. 2), and is reflected in the observed moduli of the samples. The sample with slower crosslinker 3 shows a noticeably higher elastic (G') than viscous (G") modulus throughout the range of frequencies tested, showing a high resistance to flow corroborating the relatively inert nature of the crosslinker. On the other hand, the sample crosslinked by **4** shows comparable elastic and viscous moduli in the range of tested frequencies, showing a much lower resistance to flow consistent with rapidly shuffling crosslinkers. Finally, the crossover frequency of G' and G" of crosslinker 3 sample, corresponding to its gel point, is beyond the lowest frequency tested (0.01 Hz), which is several orders of magnitude lower than the ~1 Hz crossover frequency of sample crosslinked by 4. These results corroborate the difference in rates determined in small molecule exchange and demonstrate the applicability of the concept to the gel state.

To further correlate the small molecule kinetics with dynamic properties of the solid polymer, we investigated the malleability of the samples by performing stress-relaxation studies of 20%-diol PCO crosslinked with 1.0% of either crosslinker **3** or **4** at various temperatures ranging from 35 to 55 degrees. We found, given identical crosslinking percentages, that solid polymer samples crosslinked with crosslinker **4** (Fig. 3b) released stress much faster (within 5 min for 2% strain) than samples crosslinked



Figure 3. Solution rheology and stress relaxation data. **a.** Rheological data showing storage (diamond) and loss (square) moduli for samples crosslinked with compounds **4** (unfilled) and **3** (filled). **b** & **c.** Stress relaxation data for 20%-diol PCO crosslinked with di-boronic esters **4** (b) or **3** (c).

by **3** (>20 min for 2% strain; Fig. 3c) at all temperatures, providing good evidence that variations in small molecule properties can manifest in tunable malleability for materials in the solid state. The sample containing the fast exchange boronic ester (crosslinker **4**) is significantly more malleable than the system crosslinked by the slow exchange boronic ester.

Finally, we prepared dynamically crosslinked diol PCO samples and performed self-healing experiments on these samples. Crosslinked bulk samples of 20%-diol PCO polymers were prepared using both the fast and slow di-boronic ester crosslinkers. To ensure that there were enough dynamic units present without making the material too stiff through overcrosslinking, crosslinking percentages were empirically chosen to be 0.5 and 1.0% with respect to monomer. Solution cast polymer films were concentrated in a vacuum oven and melt pressed to afford elastomeric samples (details of sample preparation and mechanical property studies are in the Supporting Information). The mechanical properties of the samples are summarized in Table 1. Despite of dramatic difference in dynamic properties, the static mechanical properties are comparable for the networks having same percentage of fast and slow exchange crosslinkers. Whereas B-N dative interaction may exist in the network with fast crosslinker 4, given the relatively weak B-N bond in this system⁴² and low density of boronic ester crosslinkers, B-N interactions should not play a significant role in the material properties. For self-healing test, we completely cut through the sample with a razor blade and gently placed the cut interfaces together for one minute and allowed them to heal for 16 hours. Due to the semicrystalline nature of the 20%-diol PCO (See Fig. S1 in the SI), a slightly elevated temperature (50 °C) was required to produce effective healing.

 Table 1. Static tensile data for dynamically crosslinked samples.

| Sample | 0.5% Fast (4) | 1.0% Fast (4) | 0.5% Slow (3) | 1.0% Slow (3) | Uncrosslinked |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-----------------|
| E ^a (pristine) | 4.68 ± 0.39 | 4.86 ± 0.86 | 4.55 ± 0.45 | 3.23 ± 0.52 | 2.23 ± 0.28 |
| E (healed) | 4.63 ± 0.32 | 4.81 ± 0.40 | 4.15 ± 0.13 | | |
| ϵ^{D} (pristine) | 345 ± 80 | 174 ± 10 | 446 ± 27 | 121 ± 31 | 1030 ± 66 |
| ε (healed) | 344 ± 160 | 158 ± 21 | 28.3 ± 7.1 | | |
| σ^{c} (pristine) | $1.85\ \pm 0.38$ | 1.51 ± 0.27 | 1.97 ± 0.36 | 1.12 ± 0.18 | 0.821 ± 0.030 |
| σ (healed) | 1.75 ± 0.35 | 1.47 ± 0.51 | 0.723 ± 0.10 | | |
| | | | | | |

^{*a*} Young's modulus calculated from the initial slope of static stress strain curves in (MPa). ^{*b*} Ultimate tensile strain (mm/mm). ^{*c*} Ultimate tensile strength (MPa).

Only the sample containing the fast crosslinker 4 was able to self-heal, almost quantitatively recovering the material's mechanical properties including Young's modulus, yield strength, ultimate tensile strain and strength (Fig. 4a&c, and Table 1). On the other hand, the sample containing the slow-exchange crosslinker 3 showed minimal or no healing (Fig. 4b&d, and Table 1). Furthermore, both uncrosslinked and permanently crosslinked (via 1,4-diisocyanatobutane) 20%-diol PCO samples did not display any healing, verifying that healing was not due to other mechanism, such as through hydrogen bonding of the diol moieties in the PCO backbone (see Figs. S3-4). Together, these results indicate that dynamic shuffling of the boronic esters is directly responsible for self-healing of our materials. Crucially, the variability in healing efficiencies follows the expected trend based on kinetics of the small molecule boronic ester transesterification reaction, directly demonstrating the effect of small molecule dynamics on emergent bulk self-healing.



Figure 4. Self-healing tests for crosslinked 20%-diol PCO. All red curves are healed samples and blue curves are pristine samples. **a.** Sample crosslinked by 0.5-mol% compound 4. **b.** Sample crosslinked by 0.5-mol% compound 3. **c.** Sample crosslinked by 1.0-mol% compound 4. **d.** Sample crosslinked by 1.0-mol% compound 3. Absence of red (self-healed) curve is due to complete lack of healing in this particular sample.

We further envisioned that the dynamic boronic ester crosslinks could allow for reprocessing of the samples. To test this, the 20%-diol PCO crosslinked sample by 0.5 mol % **4** was cut into small millimeter sized pieces and then melt pressed at 80 °C to reform the bulk materials (Fig. 5b). Static tensile tests proved that after multiple cycles, the materials were able to recover most of their mechanical properties (Fig. 5a). The thermal stability of the materials (Fig. S2) is high and remains unchanged as a result of the crosslinker, suggesting that the incorporation of boronic esters into the polymer does not decrease the thermal stability.



Figure 5. Reprocessing (three cycles) of 20%-diol PCO crosslinked by 0.5-mol% compound **4. a.** Static mechanical testing of reprocessed samples. **b.** The image on the top was the sample cut into mm sized pieces and on the bottom was the reprocessed sample after the third repetition.

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One potential issue of our design is the hydrolytic stability of boronic ester linkages. To test for this, we immersed our crosslinked samples in water overnight and then monitored any change of mass and mechanical properties. The mass change was negligible for samples before and after water submersion, indicating no appreciable transesterification and dissolution of the resulting small molecules (Table S2). Importantly mechanical properties of the samples after submersion in water over night remained unchanged (Fig. S5), further confirming the hydrolytic stability of boronic ester embedded in our polymer system. Despite the fact that small molecule boronic esters are susceptible to hydrolysis,²² the relatively hydrophobic local environment of our bulk polymer can prohibit the uptake of water into the crosslinked network, effectively shielding the boronic esters from hydrolysis. A similar observation was made for a different bulk boronic ester network reported recently.³³

In conclusion, we have demonstrated that the dynamic boronic ester linkage can be successfully used to prepare malleable, selfhealing, and reprocessable covalent network polymers. The dynamic exchange of boronic esters bonds afforded the observed dynamic properties. Significantly, tuning the rates of transesterification in the crosslinkers varied the malleability and the efficiency of self-healing, demonstrating a direct link between small molecule kinetics and rate of self-healing. This work shows the possibility of bottom-up rational design of dynamic materials with tunable dynamic properties through simple perturbations of small molecule structure and kinetics, which may give rise to materials with a variety of applications, ranging from robust selfhealing elastomers to processable thermosets.

ASSOCIATED CONTENT

Supporting Information

All experimental details including sample preparation and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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