

Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds

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S Supporting Information

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 self-healing properties of bulk materials through simple small molecule perturbations. Here we describe the use of tunable rates of boronic ester transesterification to tune the malleability and self-healing efficiencies of bulk materials. Specifically, we used two telechelic diboronic ester small molecules with variable transesterification kinetics to dynamically cross-link 1,2-diol-containing polymer backbones. The sample cross-linked 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 kinetics to dynamic properties of bulk solid material and may serve as a guide for the 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 cross-linked polymers can be reprocessed and recycled while still maintaining their thermal and chemical stability.^{1–6} Moreover, reversible covalent bonds^{7–11} and noncovalent bonds^{12–15} have been employed to design self-healing materials. While many dynamic motifs have been developed,^{7–15} 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 the dynamicity of metal–ligand,^{16–18} imine metathesis,¹⁹ and protein–ligand²⁰ interactions has been shown to impact various dynamic properties of cross-linked organogels^{16–18} and hydrogels²⁰ in solution, such a strategy has rarely been demonstrated in bulk solids for the design of malleable and self-healing materials.²¹

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

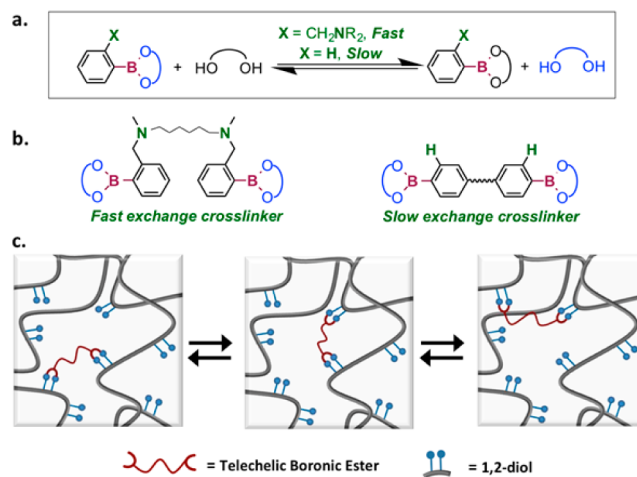


Figure 1. Design concept. (a) Tuning neighboring group to control the exchange kinetics of boronic ester. (b) Design of diboronic ester cross-linkers with tunable exchange kinetics. (c) Dynamic exchange of boronic ester cross-linkers affords dynamic materials.

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 have been largely limited to solution based systems,^{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 a self-healing bulk material utilizing boronic esters, in which the healing had to be facilitated by water to induce boronic ester hydrolysis and reformation.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, affording us the opportunity to develop a library of materials with tunable transesterification kinetics and dynamic properties.

Specifically, we demonstrated our concept with a simple polymer embedded with 1,2-diol moieties as attachment sites for boronic esters, cross-linked by telechelic divalent boronic esters. Two kinetic variants of diboronic esters were chosen to serve as dynamically mobile cross-linkers for self-healing (Figure 1).

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Consistent with our hypothesis, both cross-linked polymer networks exhibited malleability and reprocessability. However, the two 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.

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 phenylboronic acid and *o*-(dimethylaminomethyl)phenylboronic acid (compounds 1 and 2, respectively, Figure 2a), and their rates of

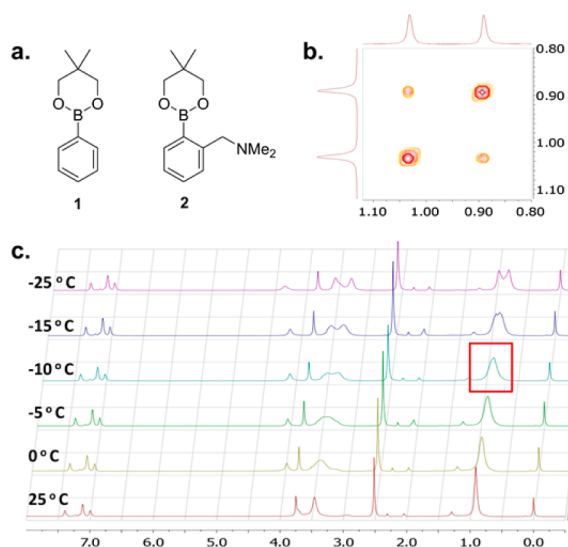
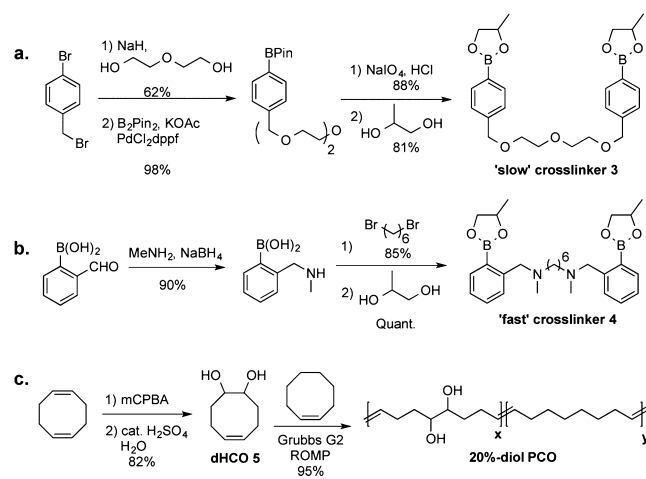


Figure 2. NMR kinetic study of boronic ester transesterification. (a) The two model compounds, slower exchanging boronic ester 1 and faster exchanging boronic ester 2. (b) EXSY results for compound 1 shows $k = 0.016 \pm 0.004 \text{ s}^{-1}$. (c) Coalescence for compound 2 shows $k \sim 3000 \text{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

self-transesterification were monitored in the presence of one 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 temperatures (Figure 2c).³⁴ The rate of transesterification was determined to be $\sim 3000 \text{ s}^{-1}$ with an activation energy of 12.6 kcal/mol. The rate of transesterification of the slower boronic ester 1 could not be monitored through coalescence and was instead determined via 2D exchange spectroscopy (EXSY)³⁵ as $0.016 \pm 0.004 \text{ s}^{-1}$ (Figure 2b). This is five orders of magnitude slower than variant 2 which has a neighboring *o*-dimethylaminomethyl group, confirming the earlier observation that the neighboring group has a strong influence on the transesterification 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 this molecular design to dynamically crosslinked polymers. First, diboronic ester cross-linkers of the slow (3) and fast (4) variants were synthesized. Cross-linker 3 was synthesized in four steps starting from 4-bromobenzyl bromide and diethylene glycol^{38–40} (Scheme 1a).

Scheme 1. Synthesis of Diboronic Ester Cross-linkers and 1,2-Diol-Containing Polycyclooctene Polymer^a



^aSynthesis of (a) “slow” diphenylboronic ester cross-linker 3, (b) “fast” di(*o*-aminophenylboronic) ester cross-linker 4, and (c) 1,2-diol-containing polycyclooctene (20%-diol PCO).

Faster exchanging cross-linker 4 was prepared in three steps from 2-formylphenylboronic acid⁴⁰ (Scheme 1b). We chose to synthesize the 1,2-diol containing polymer backbone using ring-opening metathesis polymerization (ROMP) of cyclooctene-based monomers.⁴¹ Starting from cyclooctadiene, dihydroxylated cyclooctene (dHCO) monomer 5 was prepared in two steps, which was then copolymerized with cyclooctene to afford the 1,2-diol-containing polycyclooctene polymer (20%-diol PCO) (Scheme 1c, with full details in SI).

Next, we used solution rheology to monitor the solution dynamic properties of polymer networks cross-linked by different boronic ester cross-linkers (Figure 3a). A solution of 20%-diol PCO in toluene was cross-linked with compound 3 or 4. This caused gelation in the sample with cross-linker 3, while the sample cross-linked by 4 showed only a mild increase in viscosity, which is in qualitative agreement with the small

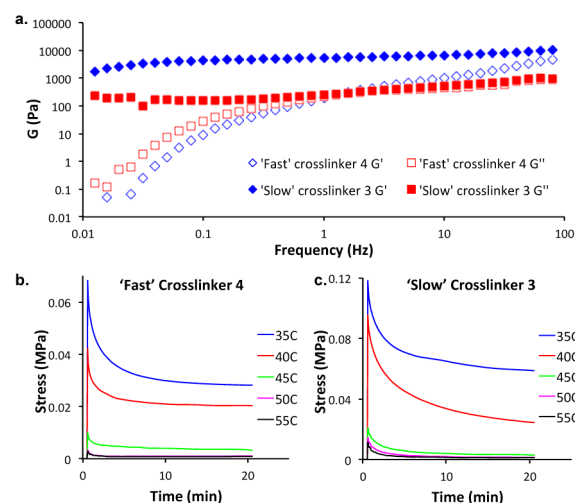


Figure 3. Solution rheology and stress relaxation data. (a) Rheological data showing storage (diamond) and loss (square) moduli for samples cross-linked with compounds 4 (unfilled) and 3 (filled). (b, c) Stress relaxation data for 20%-diol PCO cross-linked with diboronic esters 4 (b) or 3 (c).

molecule exchange kinetics (Figure 2) and is reflected in the observed moduli of the samples. The sample with slower cross-linker 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 cross-linker. On the other hand, the sample cross-linked 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 cross-linkers. Finally, the crossover frequency of G' and G'' of cross-linker 3 sample is beyond the lowest frequency tested (0.01 Hz), which is several orders of magnitude lower than the ~ 1 Hz crossover frequency of sample cross-linked 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 cross-linked with 1.0% of either cross-linker 3 or 4 at various temperatures ranging from 35 °C to 55 °C. We found that solid polymer samples cross-linked with cross-linker 4 (Figure 3b) released stress much faster (within 5 min for 2% strain) than samples cross-linked by 3 (>20 min for 2% strain; Figure 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 (cross-linker 4) is significantly more malleable than the system cross-linked by the slow exchange boronic ester.

Next, we prepared dynamically cross-linked 20%-diol PCO samples and performed self-healing experiments on these samples. Cross-linked bulk samples of 20%-diol PCO polymers were prepared using both the fast and slow diboronic ester cross-linkers. To ensure that there were enough dynamic units present without making the material too stiff through overcrosslinking, cross-linking 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 SI). The mechanical properties of the samples are summarized in Table S1. Despite dramatic difference in dynamic properties, the static mechanical properties are comparable for the networks having the same percentage of fast or slow exchange cross-linkers. Whereas B–N dative interactions may exist in the network with fast cross-linker 4, given the relatively weak B–N bond in this system⁴² and low density of boronic ester cross-linkers, B–N interactions should not play a significant role in the material's mechanical properties. To test for self-healing, we completely cut through the sample with a razor blade and gently placed the cut interfaces together for 1 min and allowed them to heal for 16 h. Due to the semicrystalline nature of the 20%-diol PCO (see Figure S1), a slightly elevated temperature (50 °C) was required to produce effective healing.

Only the sample containing the fast cross-linker 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 (Figure 4a,c and Table S1). On the other hand, the sample containing the slow cross-linker 3 showed minimal or no healing (Figure 4b,d and Table S1). Furthermore, both uncross-linked and permanently cross-linked (via 1,4-diisocyanatobutane) 20%-diol PCO samples did not display any healing, verifying that healing was

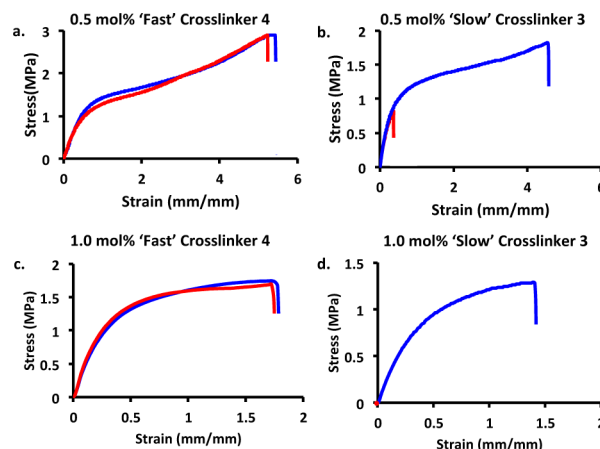


Figure 4. Self-healing tests for cross-linked 20%-diol PCO. All red curves are healed samples, and blue curves are pristine samples. (a) Sample cross-linked by 0.5-mol % compound 4. (b) Sample cross-linked by 0.5-mol % compound 3. (c) Sample cross-linked by 1.0-mol % compound 4. (d) Sample cross-linked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

not due to other mechanisms, such as through hydrogen bonding of the diol moieties in the PCO backbone (see Figures S3–4, and Table S2). 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 model study, directly demonstrating the effect of small molecule dynamics on emergent bulk self-healing.

We further envisioned that the dynamic boronic ester cross-links could allow for reprocessing of the samples. To test this, 20%-diol PCO cross-linked 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 (Figure 5b). Static tensile tests proved

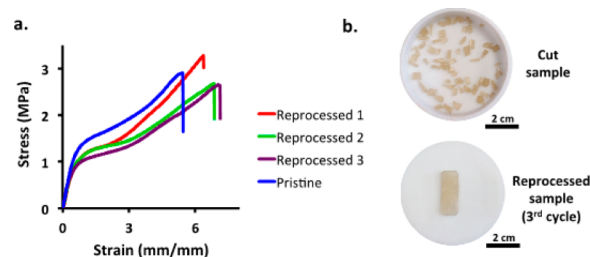


Figure 5. Reprocessing (three cycles) of 20%-diol PCO cross-linked by 0.5-mol % compound 4. (a) Static mechanical testing of reprocessed samples. (b) Top: cut sample in mm sized pieces; bottom: reprocessed sample after the third repetition.

that after multiple cycles, the materials were able to recover most of their mechanical properties (Figure 5a). The materials show high thermal stability and remain unchanged as a result of the incorporation of the boronic ester cross-linkers (Figure S2).

One potential issue of our design is the hydrolytic stability of boronic ester linkages. To test for this, we immersed our cross-linked samples in water overnight and then monitored any change of mass and mechanical properties. Neither mass nor mechanical properties were affected (Table S2, Figure S5), confirming the hydrolytic stability of the boronic ester bonds 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 cross-linked 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, self-healing, and reprocessable covalent network polymers. Significantly, tuning the rates of transesterification in the cross-linkers 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 self-healing elastomers to processable thermosets.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details including sample preparation and characterization. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03551.

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Notes

The authors declare no competing financial interest.

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